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GUIDELINES FOR DEVELOPMENT OF A
QUALITY ASSURANCE PROGRAM. VOLUME II.
GAS ANALYSIS FOR CARBON DIOXIDE, EXCESS
AIR, AND DRY MOLECULAR WEIGHT

Franklin Smith, et al

Research Triangle Institute

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Guidelines for the quality control of gas analysis for carbon dioxide, excess air, and dry molecular weight by the Federal reference method are presented. These include:

1. Good operating practices
2. Directions on how to assess performance and quality data
3. Directions on how to identify trouble and improve data quality.
4. Directions to permit design of auditing activities

The document is not a research report. It is designed for use by operating personnel.

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**GUIDELINES FOR DEVELOPMENT
OF A QUALITY ASSURANCE PROGRAM:
VOLUME II - GAS ANALYSIS
FOR CARBON DIOXIDE , EXCESS AIR,
AND DRY MOLECULAR WEIGHT**

by

Franklin Smith and Denny E. Wagoner

Research Triangle Institute
Research Triangle Park, North Carolina 27709

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EPA Project Officer: Steven M. Bromberg

Quality Assurance and Environmental Monitoring Laboratory
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ABSTRACT

Guidelines for the quality control of gas analysis for carbon dioxide, excess air, and dry molecular weight by the Federal reference method are presented. These include:

1. Good operating practices
2. Directions on how to assess performance and qualify data
3. Directions on how to identify trouble and improve data quality
4. Directions to permit design of auditing activities.

The document is not a research report. It is designed for use by operating personnel.

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SECTION I

INTRODUCTION

This document presents guidelines for developing a quality assurance program for Method 3--Gas Analysis for Carbon Dioxide, Excess Air, and Dry Molecular Weight. For convenience of reference, this method as published by the Environmental Protection Agency in the Federal Register, December 23, 1971, is reproduced as appendix A of this report.

The objectives of this quality assurance program for Method 3 are to:

- (1) Minimize systematic and random variability in the measurement process,
- (2) Provide routine indications for operating purposes of unsatisfactory performance of personnel and/or equipment,
- (3) Provide for prompt detection and correction of conditions which contribute to the collection of poor quality data, and
- (4) Collect and supply information necessary to describe the quality of the data.

To accomplish the above objectives, a quality assurance program must contain the following components:

- (1) recommended operating procedures,
- (2) routine training and evaluation of personnel and evaluation of equipment,
- (3) routine monitoring of the variables and parameters which may have a significant effect on data quality,
- (4) development of statements and evidence to qualify data and detect defects, and
- (5) action strategies to increase the level of precision/accuracy in the reported data.

Component (2) above will be treated in the final report of this contract. Component (5) will be treated in the Quality Assurance Documents (of this series) for pollutant specific methods which utilize the results of Method 2.

Implementation of a properly designed quality assurance program should enable measurement teams to achieve and maintain an acceptable level of precision in their stack gas composition measurements. It will also allow a team to report an estimate of the precision of its measurements for each source emissions test.

Variability in emission data derived from multiple tests conducted at different times includes components of variation from:

- (1) process conditions,
- (2) equipment and personnel variation in field procedures, and
- (3) equipment and personnel variation in the laboratory.

In many instances time variations in source output may be the most significant factor in the total variability. The error resulting from this component of variation is minimized by knowing the time characteristics of the source output and collecting the gas sample at a rate proportional to the stack gas velocity. The sampling period should span at least one complete output cycle when possible. If the cycle is too long, then either the sample collection should be made during a portion of the cycle representative of the cycle average or multiple samples should be collected and averaged.

Quality assurance guidelines for Method 3 as presented here are designed to insure the collection of data of acceptable quality by prevention, detection, and quantification of equipment and personnel variations in both the field and the laboratory through

- (1) recommended operating procedures as a preventive measure,
- (2) quality control checks for rapid detection of undesirable performance, and
- (3) a quality audit to independently verify the quality of the data.

This document is divided into four sections:

Section I, Introduction - The Introduction lists the overall objectives of a quality assurance program and delineates the program components necessary to accomplish the given objectives.

Section II, Operations Manual - The Operations Manual sets forth recommended operating procedures to insure the collection of data of high quality, and instructions for performing quality control checks designed to give an indication or warning that invalid data or data of poor quality are being collected, allowing for corrective action to be taken before future measurements are made.

Section III, Manual for Field Team Supervisor - The Manual for Field Team Supervisor contains directions for assessing data quality on an intrateam basis and for collecting the information necessary to detect and/or identify trouble.

Section IV, Manual for Manager of Groups of Field Teams - The Manual for Manager of Groups of Field Teams presents information

relative to the test method (a functional analysis) to identify the important operations, variables and factors, and statistical properties of and procedures for carrying out a quality audit for an independent assessment of data quality.

The scope of this document has been purposely limited to that of a field and laboratory document. Additional background information will be contained in the final report under this contract.

SECTION II

OPERATIONS MANUAL

2.0 GENERAL

This Operations Manual sets forth recommended procedures for performing stack gas analysis for carbon dioxide, excess air, and dry molecular weight according to Method 3. (Method 3 is reproduced from the Federal Register, and is included as appendix A of this document.) Quality control procedures and checks designed to give an indication or warning that invalid or poor quality data are being collected are written as part of the operating procedures and are to be performed by the operator on a routine basis. Results from certain strategic quality control checks will be used by the supervisor for the assessment of data quality.

The sequence of operations to be performed for each field test is given in figure 1. Each operation or step in the method is identified by a block. Quality checkpoints in the measurement process, for which appropriate quality control limits are assigned, are represented by blocks enclosed by heavy lines. Other quality checkpoints involve go/no-go checks and/or subjective judgments by the test team members with proper guidelines for decision making spelled out in the procedures.

The precision/accuracy of data obtained from this method depends upon equipment performance and the proficiency and conscientiousness with which the operator performs his various tasks. From equipment checks through on-site measurements, calculations, and data reporting, this method is susceptible to a variety of errors. Detailed instructions are given for minimizing or controlling equipment error, and procedures are recommended to minimize operator error. Before using this document, the operator should study Method 3 as reproduced in appendix A in detail.

It is assumed that all apparatus satisfies the reference method specifications and that the manufacturer's recommendations will be followed when using a particular item of equipment (e.g., Orsat analyzer or sampling train components).

2.1 APPARATUS REQUIREMENTS

A general description of the required apparatus along with desirable design qualities is given for grab sampling, integrated sampling, and the gas analyzer.

2.1.1 Grab-Sampling Train

2.1.1.1 General Description of the Grab-Sampling Train - A drawing of a grab-sample train is given in figure 3-1 of appendix A. Equipment specifications are given in subsection 2.1 of appendix A.

APPARATUS SELECTION

1. SELECT EQUIPMENT ACCORDING TO THE GUIDELINES GIVEN IN SUBSECTION 2.1, PAGE 4.

PRESAMPLING PREPARATION

2. INSPECT, CLEAN AND CHECK THE EQUIPMENT FOR PROPER OPERATION ACCORDING TO INSTRUCTIONS GIVEN IN SUBSECTION 2.2.1, STARTING ON PAGE 10.
3. BEFORE EVERY THIRD FIELD TEST OR EVERY THREE MONTHS, WHICHEVER COMES FIRST, PERFORM AN OPERATIONAL CHECK OF THE ANALYZER USING A SAMPLE WITH KNOWN CONCENTRATIONS AS DIRECTED IN SUBSECTION 2.2.2, PAGE 12.
4. PACK THE EQUIPMENT FOR SHIPMENT SO AS TO PRECLUDE DAMAGE WHILE IN TRANSIT.

ON-SITE MEASUREMENTS

5. ASSEMBLE THE EQUIPMENT FOR SAMPLING. VISUALLY CHECK EACH ITEM FOR POSSIBLE DAMAGE SUSTAINED DURING TRANSIT.
6. COLLECT THE GAS SAMPLE, EITHER GRAB OR INTEGRATED AS APPROPRIATE, AS DIRECTED IN SUBSECTION 2.3.1 OR 2.3.2, RESPECTIVELY.
7. PERFORM REPLICATE ANALYSES UNTIL THE PERFORMANCE CRITERIA SUGGESTED IN STEP 11 OF SUBSECTION 2.3.2 IS SATISFIED.

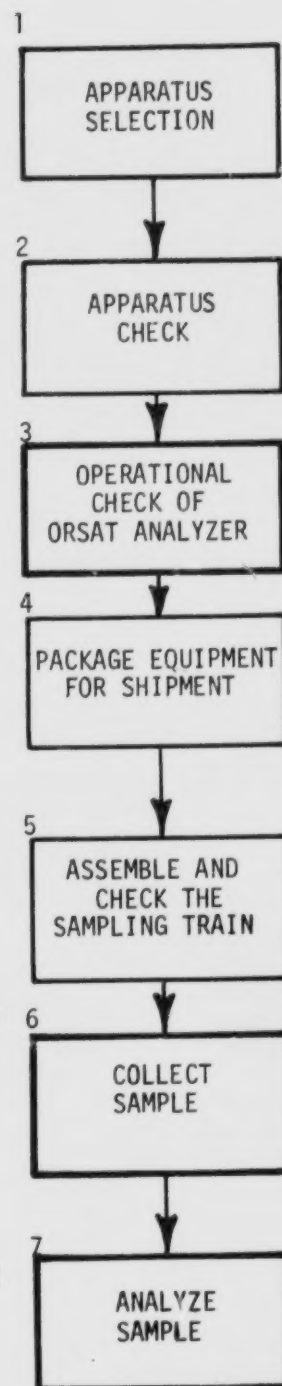


Figure 1: Operational Flow Chart of the Measurement Process

POSTSAMPLING OPERATIONS

8. COMPARE THEORETICAL AND MEASURED VALUES OF PERCENT CO₂ AND DRY MOLECULAR WEIGHT AS DIRECTED IN SUBSECTION 2.4.1, PAGE 20.
9. DISASSEMBLE AND VISUALLY INSPECT THE EQUIPMENT FOR POSSIBLE DAMAGE SUSTAINED DURING THE FIELD TEST. DOCUMENT THE DAMAGE AND ESTIMATE ITS EFFECT ON THE MEASURED VALUES.
10. PACK THE EQUIPMENT FOR SHIPMENT TO THE HOME LABORATORY.
11. PERFORM CALCULATIONS FOR THE COMPONENT GASES AND FOR THE DRY MOLECULAR WEIGHT OF THE STACK GAS.
12. FORWARD THE DATA FOR FURTHER INTERNAL REVIEW OR TO THE USER.



Figure 1: Operational Flow Chart of the Measurement Process (Continued).

2.1.1.2 Desirable Design Qualities - The probe tip should be designed so as to prevent the glass wool filter from being drawn from the probe when sampling a source that has substantial negative pressure.

Even though a one-way squeeze bulb is acceptable as a pump and in certain constrained environments may have to be used, it is recommended that, if possible, a leak-free diaphragm-type pump be used in the train.

2.1.2 Integrated Gas-Sampling Train

2.1.2.1 General Description of the Integrated Gas-Sampling Train - A drawing of an integrated gas-sampling train is given in figure 3-2 of appendix A. Equipment specifications are given in subsection 2.2 of appendix A. Specifications of and directions for using the Type-S pitot tube are given in the Quality Assurance Document of this series for Method 2.

2.1.2.2 Desirable Design Qualities - No volume specifications are given for the air-cooled condenser in the sampling train. The main consideration is that the condenser volume be kept to the minimum necessary to sufficiently cool the sample air. This is important because the larger the volume the more difficult it is to completely purge the sampling train before collecting a sample.

An alternate means of cooling the sample air requiring less volume would be to use a midjet impinger in an ice bath as a condenser. The impinger tip should be well above water level for this purpose.

2.1.3 Gas Analyzer (Orsat)

The Orsat analyzer is used to determine the stack gas composition in terms of CO_2 , O_2 , and CO concentrations. A sample is analyzed by successively passing it through absorbents that remove specific gaseous components. The difference in gas volume before and after the absorption represents the amount of the constituent gas in the sample. Constant pressure and temperature must be maintained throughout the analysis. Results are reported on a dry, volume percentage basis.

2.1.3.1 General Description - The Orsat analyzer is illustrated in figure 2. The apparatus consists basically of a glass burette to measure gas volume, a water jacket to maintain constant temperature, a glass manifold to control the flow of gases, three absorption pipettes, and a leveling bottle to move the gases. The apparatus is usually assembled inside a case equipped with front and rear doors and a carrying handle.

In this document two Orsat analyzer designs taken to represent the extremes in obtainable precision are referred to as a standard Orsat analyzer and a modified Orsat analyzer. The standard Orsat analyzer, as used herein, implies an analyzer containing a burette with 0.2 ml divisions with a

spacing between divisions of about 1 mm. The modified Orsat analyzer, on the other hand, implies an analyzer equipped with a burette having 0.1 ml divisions with the spacing between divisions being 1 mm or more.

2.1.3.2 Desirable Design Qualities - There is a wide variety of Orsat analyzer designs on the market. Some specific design features increase the precision and accuracy attainable with an Orsat analyzer. Some of these design features are:

- (1) Precision and perhaps accuracy are improved with a glass burette configuration as shown in figure 2. That is, the burette is designed with a large diameter column having a volume of approximately 75 ml joined onto a portion of a 25 ml burette graduated in 0.1 ml divisions. Such a design should result in less error in leveling the liquids and in interpolating readings on the burette than with burettes not as finely graduated and with less spacing between divisions (ref. 1). This design is referred to as a modified Orsat analyzer throughout this document.
- (2) The volume reference mark should be located on the capillary tubing at the top of the glass burette (fig. 2) as opposed to being on the larger diameter burette. Having the reference mark on a small bore capillary tube increases the precision with which the total sample volume can be determined from test to test. Also, it should result in a more accurate burette calibration and thus a more accurate sample volume determination.
- (3) The glass manifold should have as small a volume as possible to reduce the possibility of diluting the sample due to incomplete purging of the manifold. It also minimizes the increase in sample volume (i.e., the volume of gas in the manifold between the reference mark on the burette and the pipette is small).
- (4) The Orsat apparatus and case should be designed so that the leveling bottle and glass burette can be viewed side by side when leveling the liquid. The liquid levels in the burette and the leveling bottle must be the same when reading volumes; otherwise, the sample air will not be at atmospheric pressure.
- (5) The inlet sample valve (see figure 2) should be a three-way valve to allow purging of the manifold without causing the sample bag or inlet gas to be diluted by ambient air.

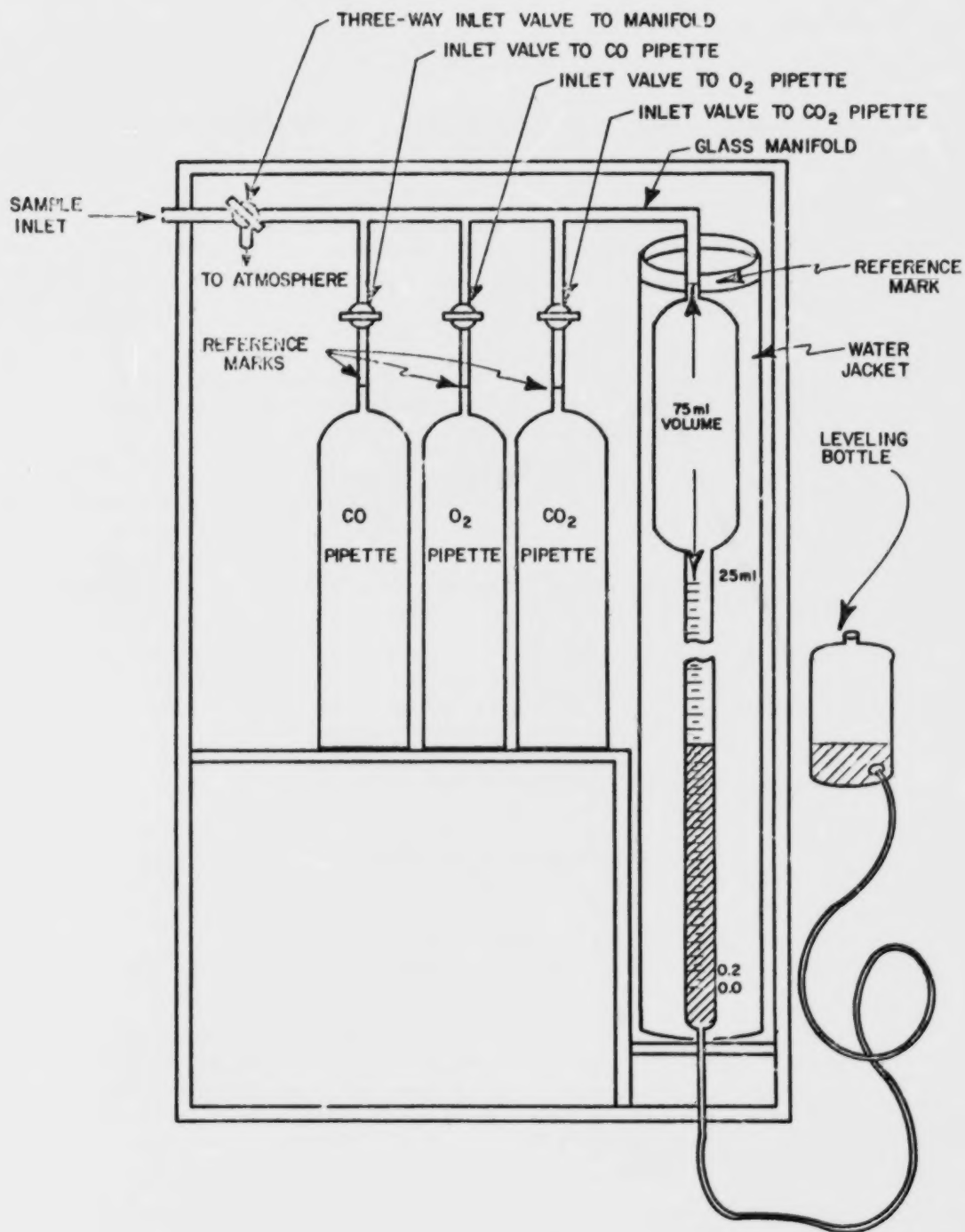


Figure 2: Illustration of Key Components of an Orsat Analyzer for Measuring CO_2 , O_2 , and CO Contents of Stack Gases

2.2 PRESAMPLING PREPARATION

2.2.1 Apparatus Check

2.2.1.1 Grab Sample (figure 3-1, Appendix A) - The grab-sample train should be checked as follows:

- (1) The probe should be visually checked for signs of leaks. A glass probe will be either broken or cracked, and a stainless steel probe will be corroded as an indication of leaking. The probe should be cleaned and both ends capped.
- (2) The pump, either a one-way squeeze bulb or leak-free diaphragm type pump, should be checked to see if it is operating properly. All connectors and tubing should be checked for leaks. This can be done by slightly pressurizing the system and checking for leaks by applying soap bubbles to the connections and joints and observing to see if the bubbles burst more rapidly than normal.

2.2.1.2 Integrated Sample (figure 3-2, Appendix A) - The integrated-gas sampling train should be checked as follows:

- (1) The probe should be cleaned with soap and water, rinsed with distilled water and allowed to dry. It should be visually checked for leaks. A glass probe will be either broken or cracked, and a stainless steel probe will show signs of corroding if leaking. Both ends of the probe should be capped to prevent contaminants from entering the probe while not in use.
- (2) The air-cooled condenser or equivalent should be cleaned and leak checked.
- (3) The needle valve and rotameter should be disassembled, cleaned, and reassembled at any sign of foreign matter in the rotameter or erratic behavior of the rotameter.
- (4) Leak test the Tedlar bag by filling it with air (under a slight pressure), sealing, and letting sit overnight. If there is any visual indication of collapsing, do not use it for the field test. It is recommended that the bag be mounted in a rigid container to prevent puncture when in the field.
- (5) Service the pump according to the manufacturer's directions. Check the motor for proper electrical grounding, i.e., use a three-wire system.

2.2.1.3 Gas Analyzer (Orsat) - An Orsat analyzer or its equivalent is utilized in the determination of CO_2 , O_2 , and, if desired, CO . The Orsat should be checked and serviced before each field test in the following manner:

- (1) The solution used in the leveling should be distilled water containing approximately 5 percent by volume of concentrated sulfuric acid (2 or 3 ml of methyl orange indicator is usually added to indicate that the solution is acidic). The solution is then saturated with a salt, usually sodium sulfite or sodium chloride, at the temperature at which the Orsat is expected to operate. The sulfuric acid acts as a drying agent to remove any moisture from the sample and the saturated salt solution prevents the absorption of sample gases by the leveling solution. This should be prepared as a stock solution and checked before each field test or prepared fresh for each field test.
- (2) Absorbing solutions should be changed if more than 10 passes are needed to obtain a constant reading for any component gas.

Charge the Orsat analyzer when applicable (following the manufacturer's instructions) with fresh absorbing reagents. Any absorbing reagent can be used if it does not react with other gases in the sample (i.e., not subject to interferences) and is quantitative for the component gas being analyzed. Some commonly used absorbents are:

Absorbent	Gas
Potassium hydroxide	CO_2
Alkaline pyrogalllic acid, chromous chloride, or equivalent	O_2
Acid cuprous chloride over copper strips, cuprous sulfate 1-beta naphthol, or equivalent	CO

- (3) The stopcocks should be removed and cleaned. Stopcock grease should be carefully applied so as to insure a leak-free system and to preclude plugging the air passages. Stopcocks are generally not interchangeable. Replace each one in the same port that it was originally removed from.

(4) Assemble the Orsat analyzer and check for leaks as follows:

- (a) According to the manufacturer's procedures appropriate to the Orsat being used, adjust the level of each absorbing reagent to its reference mark (see fig. 2); then close the stopcock to that pipette.
- (b) With the sample inlet valve open, lower the liquid level in the glass burette to near the 0.0 ml mark. Close the sample inlet valve (stopcock) and set the leveling bottle on top of the Orsat case. This pressurizes the sample air in the burette and manifold.
- (c) Observe the analyzer in this position for 10 to 15 minutes after the liquid level in the burette has stabilized. If there are no leaks, all absorbing solution levels should remain at their respective reference marks and the liquid level in the burette should remain fixed once it has stabilized after placing the leveling bottle on the top of the case.

If leaks are present, they must be eliminated before performing a field test.

2.2.2 Calibration Check of the Orsat Analyzer

It is recommended that the following calibration check be performed before every third field test or before any field test in which the Orsat analyzer has not been checked during the previous 3 months.

To check the O_2 absorbing reagent and the operating technique of the operator, it is recommended that the percent of O_2 in air be determined.

The average of three replicates should be 20.8 ± 0.7 percent when using the standard Orsat and 20.8 ± 0.35 when using a modified Orsat. A measured average value higher than 21.5 percent indicates poor operator technique, while a value lower than 20.1 percent indicates leaking valves, spent absorbing reagent (for O_2 only), and/or poor operator technique. (See subsection 4.1 for the derivation of the above limits.)

A more thorough check that could be made if the required equipment is available is to sample from a manifold containing a known mixture of CO , CO_2 , and air. This is applicable to grab samples or by the integrated bag technique. In both cases the sample is analyzed for CO , CO_2 , and O_2 using the Orsat analyzer. The average of three replicates should be within

approximately 0.7 percent (absolute) of the known concentration of each gas (or 0.35 percent when using the modified Orsat). Again, high measured values indicate poor operator technique, while low values indicate leaking valves, spent absorbing reagent, and/or poor operator technique.

If the above limits are exceeded, corrective action in the form of equipment maintenance and/or operator training should be taken.

2.2.3 Package Equipment for Shipment

This aspect of the test method in terms of logistics, time of sampling, and quality of data is very dependent upon the packing of the equipment in regards to (1) accessibility in the field, (2) ease of movement on site, and (3) optimum functioning of sampling and analytical devices in the field. Equipment should be packed under the assumption that it will receive severe treatment during shipment and field operation. Each item should be packaged as follows:

- (1) Probes, pumps, and condenser should be packed in cases or wooden boxes filled with packing material or lined with styrofoam.
- (2) Rotameters, needle valves, and all small glass parts should be individually packed in a shipping container.
- (3) For integrated samples, it is advantageous that the rigid container for the sampling bag serve also as its shipping container.
- (4) The Orsat should be disassembled and each item individually packed in suitable packing material and rigid containers. It is recommended that spare parts and absorbent solution be shipped in another shipping container.

2.3 ON-SITE MEASUREMENTS

The equipment, i.e., the sampling train and Orsat analyzer, are unpacked at the sampling site and visually inspected for any damage that might have been sustained during shipment from the laboratory.

It is suggested that, if at all possible, a nearby laboratory or room should be utilized for conducting the gas analysis. The Orsat analyzer should be used in the stack area as a last resort only. Accuracy and precision will nearly always be enhanced by moving to a laboratory for analysis.

Assemble the Orsat analyzer and check for leaks as directed in subsection 2.2.1.3, step 4.

Special precautions to observe when using an Orsat analyzer for gas analysis are as follows:

- (1) No ambient air must be allowed to enter the Orsat analyzer during testing.
- (2) The gas must always be sampled in the following sequence:

Absorber No. 1 - CO_2

Absorber No. 2 - O_2

Absorber No. 3 - CO .

This is necessary because Absorber No. 2 will also absorb CO_2 and Absorber No. 3 will absorb O_2 and possibly CO_2 , resulting in erroneous data.

- (3) Solution in the burette must be saturated with the salt at the operating temperature, or absorption of sample gases prior to analysis will occur. Also, the solution should be acidic (as indicated by the methyl orange indicator) to absorb any moisture in the sample gas.
- (4) Absorber solution must be kept from entering the capillary column manifold. If solution enters the manifold, the test should be voided and the sample manifold cleaned. Acetone can be utilized in this cleanup.
- (5) Gas samples must be allowed to come to temperature equilibrium with the water jacket before analysis. A minimum of 5 minutes should be allowed for equilibration.
- (6) The data yields the molecular weight of the gas on a dry basis and should be treated as such in future calculations.
- (7) In placing the probe in the stack in any sampling method, precautions should be taken to prevent dilution of the stack gas by an influx of ambient air, i.e., if a negative pressure exists in the stack.
- (8) An Orsat analyzer must operate under constant temperature and pressure; therefore, it is necessary when a reading is taken from the Orsat analyzer that the levels of solution in the burette and leveling bottle be the same to insure equal pressure. The water jacket acts as a buffer for temperature changes.

- (9) If the source being tested is known to have or is suspected of having a high SO_2 concentration, it should be measured quantitatively as by Method 6 and subtracted from the CO_2 determinations. Measurement and subsequent corrections should be made when the SO_2 level is suspected of being as much as 3 percent (relative) of the CO_2 concentration when the data are to be used to correct particulate emission rates to 12 percent CO_2 . If the data are to be used just for calculating the molecular weight, then interferences as high as 0.5 percent (absolute) or 5,000 ppm from SO_2 are acceptable (this level of interference will result in an error of only about 0.1 lb/lb-mole in M_d).

2.3.1 Grab Sampling

Set up the grab-sampling train as depicted in Figure 3-1 of Appendix A. Visually check each connection for possible leaks.

- (1) Place the probe in the stack with the probe tip at least 12 inches from the stack wall.
- (2) Plug the sampling port as well as possible with a sponge or rag to prevent dilution of the stack gas by ambient air if the stack pressure is negative.
- (3) Purge the sampling train several times if a one-way squeeze bulb is used, or for a few seconds if a leak-free diaphragm-type pump is used.
- (4) It is recommended that, if at all possible, a flexible bag be used to collect the sample and that this bag be transported to a laboratory for analysis.
- (5) Draw sample gas into the analyzer and flush (i.e., allow to bubble through the burette solution) at least three times to saturate the liquid in the burette with the gas being analyzed and to insure that the air remaining in the manifold is of the same composition as the sample to be analyzed.

Caution: Once the flushing operation has begun, ambient air must not be allowed to enter the manifold.

- (6) Draw in a fixed volume (usually 100 ml) of the sample air following the manufacturer's instructions. Allow a minimum of 5 minutes for the sample air to come to a temperature equilibrium with the water jacket around the burette (unless the sample and the analyzer have both been at the same temperature for a longer period of time).

- (7) Proceed with the sequential determination of CO_2 , O_2 , and CO as directed by the instructions supplied by the manufacturer of the gas analyzer.

Note: If more than 10 passes are required to reach a constant reading for any one of the component gases, the applicable absorbing reagent should be replaced.

- (8) The Reference Method specifies that steps 4 through 7 be repeated until three consecutive analyses vary no more than 0.5 percent (absolute) by volume for each component gas being analyzed. Since results from collaborative tests (refs. 1,2) indicate a standard deviation of approximately 0.4 percent (absolute), the above criteria could be difficult to satisfy. Also, the molecular weight determination is shown to be relatively insensitive to gaseous component measurement errors (see subsection 4.1.1.1). Therefore, it is recommended here that the average of the first three consecutive analyses--where the range, R , (i.e., the difference in the largest and smallest values) for each of the component gases is not greater than 1.74 percent (absolute) or 0.87 percent (absolute) when using the modified Orsat analyzer--be used. See subsection 4.1 for a discussion of these limits.

- (9) Fill in the information required and the test data on an Orsat Field Data Sheet as shown in figure 3.

2.3.2 Integrated Sampling

Integrated sampling specifies sampling at a rate proportional to the stack gas velocity. This requires the use of a type-S pitot tube or equivalent to monitor the stack gas velocity. Directions for the care and use of the type-S pitot are given in the Quality Assurance Document of this series for Method 2.

The procedure for collecting an integrated sample is as follows:

- (1) Evacuate the flexible bag. This can be accomplished by connecting one end of a piece of flexible tubing equipped with a quick disconnect to the flexible bag and the other end to the intake side of the sampling train pump.
- (2) Set up the integrated gas-sampling train as shown in figure 3-2 of appendix A, except do not connect the flexible bag.

FIELD TEST IDENTIFICATION INFORMATION

Location _____ Comments: _____
 Date _____
 Time _____
 Operator _____
 Date* () _____
 Reagents Used (CO₂), (O₂), (CO)

MEASURED RESULTS

Average: %CO₂ _____ %O₂ _____
 %CO _____ M_d _____

THEORETICAL RESULTS

%CO₂ _____ %O₂ _____
 %CO _____ M_d _____ lb/lb-mole

RECORDED FIELD DATA

Replicate Number	Original Volume Reading 1	(CO ₂) Reading 2 (ml)	(CO ₂) Volume (2-1) (ml)	(O ₂) Reading 3 (ml)	(O ₂) Volume (3-2) (ml)	(CO) Reading 4 (ml)	(CO) Volume (4-3) (ml)

*Date that the absorbing reagents were replaced.

Figure 3. Sample Orsat Field Data Sheet

- (3) Visually and physically inspect each connection to insure that they are tight and leak-free.
- (4) Insert a plug of borosilicate (Pyrex) filtering fiber (glass wool) into the inlet end of the probe to filter out particulates.
- (5) Place the probe in the stack with the probe end at least 12 inches from the stack wall, and plug the sampling port as well as possible (if the stack gas has a positive pressure and there are hot and/or noxious gases, a packing gland should be used on the sampling port to prevent the escape of these gases).
- (6) With the flexible bag still disconnected, purge the sampling train by running the pump for a sufficient time to completely purge the system, especially the air-cooled condenser. The minimum purging time should be such that a volume of sample gas at least as large as three times the volume of the sampling train including the condenser will pass through the train.
- (7) With the pump turned off, connect the sampling train to the flexible bag.
- (8) Sample at a rate proportional to the stack gas velocity as monitored by a type-S pitot tube. The rate of sampling is varied according to the variation of the square root of the velocity pressure differential, i.e., sampling rate as indicated by the rate meter is set and subsequently adjusted according to the values of $\sqrt{\Delta P}$.
- (9) Disconnect the flexible sampling bag and remove to a suitable area for performing the Orsat analysis. The collected sample should be allowed to sit for about 30 minutes to insure thorough mixing and temperature equilibrium. It is recommended that the analysis be performed as soon as practical after the 30-minute waiting period. Although no undesirable effects have been reported for stored samples, a delay in analysis of more than 8 hours should be avoided if possible.
- (10) Following the instructions supplied by the manufacturer, connect the Orsat analyzer to the sample bag and purge the manifold, saturate the liquid in the burette with sampling gas, and draw in the desired volume of sample as discussed in steps 4 through 7 of subsection 2.3.1, "Grab Sampling".

- (11) The Reference Method specifies that the analysis be repeated until three consecutive analyses vary no more than 0.2 percent by volume for each component gas being analyzed. This performance criteria may be difficult to achieve (ref. 2). It is suggested here that the following criteria be used:
- (a) When the data are to be used for computing the stack gas molecular weight, accept the average of the first three consecutive analyses where the range, R , (i.e., the difference in the largest and smallest values) for each of the component gases is not greater than 1.74 percent (0.87 percent for modified Orsat). (Note that a CO measurement is not used in calculating molecular weight (see subsection 2.4.4.2).) This is consistent with the repeatability obtained in a collaborative test using standard Orsat analyzers (ref. 2). See section 3.2 for a discussion of this point. This range limit implies that the average of the three analyses is within ± 1 percent (absolute) of the true value (≈ 0.5 percent for the modified Orsat) about 98 percent of the time (see subsection 4.1) and, subsequently, the calculated molecular weight would be in error by no more than about 1.5 percent (relative) or about 0.75 percent when using the modified Orsat.
 - (b) When the data are to be used to correct the particulate emissions level of incinerators to 12 percent CO_2 as well as to determine the dry molecular weight, the following procedures are recommended:
 - (1) Perform three replicate analyses. Use the averages of the three replicates for $\%\text{O}_2$ and $\%\text{CO}$ if the ranges are within the limits given in (a) above.
 - (2) For $\%\text{CO}_2$ compute the average, $\overline{\%\text{CO}_2}$, from the three replicates. From figure 6, page 42, determine the required number of replicates, r , in accordance with the type of Orsat being used. The solid curve is applicable when a standard Orsat with 0.2 ml divisions is used, and the dashed curve when an Orsat with 0.1 ml divisions (modified Orsat) is used.
 - (3) Counting the original three replicates, perform any additional replicates as determined above.

- (4) Accept the average of the r replicates as the true value if their range, R , satisfies the criteria given in Table 1 of Section III under 1(b), page 29.

If the criterion of (4) cannot be met, corrective action in the form of replacing the absorbing reagent or having the analyses repeated by another operator should be taken.

2.4 POSTSAMPLING OPERATIONS

2.4.1 Compare Measured Values Against Theoretical Values

After the analyses have been performed and before the equipment is disassembled, the measured and theoretical results should be compared as a quick check for gross measurement error.

Combustion nomographs are available commercially (ref. 3) for estimating the percent by volume of CO_2 , CO , and O_2 when the fuel composition is known. Also, the molecular weight of the stack gas can be calculated using the nomographs.

Perform the calculations on the measured data as directed in subsection 2.4.4, "Calculations". The following comparisons are suggested:

- (1) If the measured data are to be used for determining the stack gas molecular weight only, compare the estimated dry gas molecular weight, M_{de} , and the measured M_{dm} by

$$D_{M_d} = M_{dm} - M_{de}$$

where D_{M_d} = Difference in measured and estimated values, lb/lb-mole,*

M_{dm} = The measured value as calculated in Subsection 2.4.4.2, lb/lb-mole, and

M_{de} = The estimated value using the combustion nomograph, lb/lb-mole.

If D_{M_d} is less than 0.6 lb/lb-mole, accept the measured value; otherwise, it is recommended that another sample be drawn from the stack and analyzed. The average of the two measurements is used in subsequent calculations. Theoretical values should be recorded on the form in figure 3.

*Molecular weight is numerically the same in lb/lb-mole, g/g-mole, or Kg/Kg-mole, etc.

- (2) If the measured data are to be used to correct particulate emission levels to 12 percent CO₂ in addition to the comparison given in (1) above, perform the following comparison:

$$D_{CO_2} = \%CO_{2m} - \%CO_{2e}$$

where D_{CO_2} = Difference in measured and estimated values, percent,

CO_{2m} = Measured CO₂ in percent (average of r replicates), and

CO_{2e} = Estimated or theoretical CO₂ in percent.

Accept the measured value if D_{CO_2} is less than 2 percent (absolute); otherwise, check the equipment and technique then collect and analyze r more samples. (Note: Some judgment has to be made by the supervisor as to how good the process information is before repeating the analysis.)

Record the estimated or theoretical values on the form in figure 3 (these theoretical calculations could have been made and recorded before the field test if sufficient prior knowledge of the process were available).

2.4.2 Disassemble and Inspect Equipment

When disassembling the equipment, it is important to visually inspect the sampling train components and the Orsat analyzer for any signs of damage that could have adversely affected the measured values.

Any identified damage that was not detected during the test should be documented on the field data sheet and thoroughly evaluated, by performing the appropriate apparatus check as directed in subsection 2.2.1, when back in the laboratory. If after checking it is concluded that the damage could have biased the measurements, a description of the damage and an estimate of direction and magnitude of potential bias in the data should be a part of the field test report. If possible, repeat the field test.

2.4.3 Pack Equipment for Shipment to Laboratory

Pack the equipment for shipment to the laboratory in the same manner described in subsection 2.2.3. Also, the data sheets, which have been prepared in duplicate, are returned to the laboratory; one copy by mail and one copy hand-carried.

2.4.4 Calculations

2.4.4.1 Component Gases - Compute the average value for each of the component gases from the r consecutive analyses satisfying the suggested performance criteria given in subsection 2.4.1. Round each average to the nearest 0.01 percent. (The Reference Method says to report to the nearest 0.1 percent; it is felt that averaging three or more values justifies rounding to 0.01 percent through intermediate calculations, and the final molecular weight will be rounded to the first decimal.) Record the averages on the form in figure 3 in the spaces for Measured Values.

2.4.4.2 Dry Molecular Weight - Compute the average measured molecular weight of the stack gas on a dry basis by

$$\bar{M}_{dm} = 0.44 (\overline{\%CO_2}) + 0.32 (\overline{\%O_2}) + 0.28 (\%N_2 + \%CO)$$

where $\bar{M}_{dm}$ = The average measured dry molecular weight,
lb/lb-mole,

$\overline{\%CO_2}$ = Percent CO_2 taken as average of three
analyses, percent,

$\overline{\%O_2}$ = Percent O_2 taken as average of three
analyses, percent, and

$$(\%N_2 + \%CO) = 100 - (\overline{\%CO_2} + \overline{\%O_2}), \text{ percent.}$$

Round $\bar{M}_{dm}$ to the nearest 0.1 lb/lb-mole. Record the value as M_d on the form in figure 3, page 17. File a copy of the completed form in the laboratory log book and forward the original for further internal review or to the user.

SECTION III

MANUAL FOR FIELD TEAM SUPERVISOR

3.0 GENERAL

The term "supervisor" as used in this document applies to the individual in charge of a field team. He is directly responsible for the validity and the quality of the field data collected by his team. He may be a member of an organization that performs source sampling under contract to government or industry, a government agency performing source sampling, or an industry performing its own source sampling activities.

It is the responsibility of the supervisor to identify sources of uncertainty or error in the measurement process for specified situations and, if possible, to eliminate or minimize them by applying appropriate quality control procedures to assure that the data collected are of acceptable quality. Specific actions and operations required of the supervisor for a viable quality assurance program are summarized in the following listing.

(1) Monitor/Control Data Quality

- (a) Direct the field team in performing field tests according to the procedures given in the Operations Manual.
- (b) Perform or qualify results of the quality control checks (i.e., assure that checks are valid).
- (c) Perform necessary calculations and compare quality control checks to suggested performance criteria.
- (d) Make corrections or alter operations when suggested performance criteria are exceeded.
- (e) Forward qualified data for additional internal review or to user.

(2) Routine Operation

- (a) Obtain from team members immediate reports of suspicious data or malfunctions. Initiate corrective action or, if necessary, specify special checks to determine the trouble; then take corrective action.
- (b) Examine the team's log books periodically for completeness and adherence to operating procedures.
- (c) Approve data sheets, data from calibration checks, etc., for filing.

(3) Evaluation of Operations

- (a) Evaluate available alternative(s) for accomplishing a given objective in light of experience and needs,
- (b) Evaluate operator training/instructional needs for specific operations.

Consistent with the realization of the objectives of a quality assurance program as given in section I, this section provides the supervisor with brief guidelines and directions for:

- (1) collection of information necessary for assessing data quality on an intrateam basis;
- (2) isolation, evaluation, and monitoring of major components of system error;
- (3) collection and analysis of information necessary for controlling data quality.

3.1 ASSESSMENT OF DATA QUALITY (INTRATEAM)

Intrateam or within-team assessment of data quality as discussed herein provides for an estimate of the precision of the measurements made by a particular field team utilizing an Orsat analyzer. Precision in this case refers to replicability, i.e., the variability among replicates and is expressed as a standard deviation. This technique does not provide the information necessary for estimating measurement bias (see subsection 4.1.2 for a discussion of bias) which might occur, for example, from failure to collect a representative sample, sampling train leaks, or inadvertent exposure of the sample to ambient air. However, if the operating procedures given in the Operations Manual (section II) are followed, the bias should be small in most cases. The performance of an independent quality audit that would make possible an interteam assessment of data quality is suggested and discussed in subsection 4.2 of the Manual for Manager of Groups of Field Teams.

3.1.1 Treatment of Information

The field data are used to derive a confidence interval for the reported data. The two measurements of interest here are the dry molecular weight and the percent CO₂ measurements. Both measurements are reported when testing incinerators for particulate emissions; otherwise, only dry molecular weight is reported.

3.1.1.1 Calculating the Precision of Dry Molecular Weight Determinations - Using the first three consecutive analyses that satisfy the range criteria given in Table 1, page 29, compute three dry molecular weight values using the relationship

$$M_d = 0.44 (X_{CO_2}) + 0.32 (X_{O_2}) + 0.28 (100 - X_{CO_2} - X_{O_2})$$

where

M_d = Dry molecular weight of the sample gas, lb/lb-mole, and

X_{CO_2} and X_{O_2} = The measured values of CO_2 and O_2 , respectively, for the same replicate, percent (absolute).

Calculate the standard deviation of the three M_d values by

$$s\{M_d\} = \left[\frac{(M_{d1} - \bar{M}_d)^2 + (M_{d2} - \bar{M}_d)^2 + (M_{d3} - \bar{M}_d)^2}{2} \right]^{1/2}$$

where

$s\{M_d\}$ = Sample standard deviation calculated from three replicates, lb/lb-mole.

$M_{d1}(M_{d2})(M_{d3})$ = Dry molecular weight for replicate 1 (2) (3), lb/lb-mole.

$\bar{M}_d$ = Average dry molecular weight for three replicates, i.e., $1/3(M_{d1} + M_{d2} + M_{d3})$, lb/lb-mole.

The estimated standard deviation of the average dry molecular weight becomes,

$$\sigma(\bar{M}_d) = s\{M_d\}/\sqrt{3} =$$

based on three replicates.

3.1.1.2 Calculating the Precision of CO_2 Measurements - Precision of the CO_2 measurements should be calculated and reported when the data are to be used for correcting particulate emissions from an incinerator to 12 percent CO_2 .

An estimate of the standard deviation is calculated from the r replicates by

$$s\{\%CO_2\} = \left[\frac{(\%CO_{2_1} - \overline{\%CO_2})^2 + (\%CO_{2_2} - \overline{\%CO_2})^2 + \dots + (\%CO_{2_r} - \overline{\%CO_2})^2}{r - 1} \right]^{1/2}$$

where

$s\{\%CO_2\}$ = Sample standard deviation calculated from r replicates, percent.

$\%CO_{2_1}$ ($\%CO_{2_2}$) $\dots$ ($\%CO_{2_r}$) = Percent CO_2 measured by replicate 1(2) $\dots$ (r), percent.

$\overline{\%CO_2}$ = Average percent CO_2 for r replicates, i.e., $\overline{\%CO_2} = 1/r (\%CO_{2_1} + \%CO_{2_2} + \dots + \%CO_{2_r})$.

The estimated standard deviation of the average percent CO_2 is given by

$$\delta\{\%CO_2\} = s\{\%CO_2\}/\sqrt{r}$$

based on r replicates.

3.1.2 Reporting Data Quality

Stack gas molecular weight and, in some cases the percent CO_2 as measured by this method, are used in conjunction with pollutant specific methods to arrive at average emissions levels for those pollutants. When reported as individual quantities, they should be accompanied with precision statements.

3.1.2.1 Reporting Dry Molecular Weights - It is recommended that the average measured dry molecular weight be reported with 90 percent confidence limits. Assuming that $\bar{M}_{dm}$ is normally distributed (this is usually a valid assumption since sample means tend to be normally distributed even for nonnormal parent distributions) and using $\delta\{\bar{M}_{dm}\}$ as calculated above to estimate the standard deviation, exact confidence limits can be calculated for the true M_d value using the Student t -distribution with $r - 1 = 2$ degrees of freedom. This assumes no bias in the average values. The average measured value with 90 percent confidence limits would be

$$\bar{M}_{dm} \pm 2.92 \delta(\bar{M}_{dm})$$

where $\bar{M}_{dm}$ = The average of three replicates, lb/lb-mole,
 $\delta(\bar{M}_{dm})$ = The estimated standard deviation of $\bar{M}_{dm}$ based
on three replicates, lb/lb-mole, and
2.92 = 95th percentile of the Student t-distribution
with 2 degrees of freedom which yields a
90 percent confidence interval.

For example, if $\delta(\bar{M}_{dm})$ was calculated to be 0.14 lb/lb-mole, the reported
value with 90 percent confidence limits would be

$$\bar{M}_{dm} \pm 0.41 \text{ lb/lb-mole.}$$

The utility of the above statement follows from the fact that if this
procedure for computing confidence limits is followed, then 90 percent of
the time the true M_d value will be contained within the given limits
(assuming that $\bar{M}_{dm}$ is not biased).

3.1.2.2 Reporting CO₂ Measurements - Precision of CO₂ measurements is
reported only when the measurements are to be used to correct particulate
emissions of an incinerator to 12 percent CO₂. The same procedure as that
used for calculating the precision for M_d is used for calculating the
precision of CO₂ measurements, except the number of replicates is not
fixed at three. The average measured value of r replicates with 90 percent
confidence limits would be

$$\overline{\%CO_2} \pm t_{0.05} \delta(\overline{\%CO_2}), \text{ for } r - 1 \text{ degrees of freedom}$$

where $\overline{\%CO_2}$ = Average percent CO₂ from r replicates,
percent (absolute),

$\delta(\overline{\%CO_2})$ = The estimated standard deviation of $\overline{\%CO_2}$
based on r replicates, percent (absolute),
and

$t_{0.05}$ = 95th percentile of the Student t-distribution
with r - 1 degrees of freedom which yields a
90 percent confidence interval.

Values of $t_{0.05}$ for $r - 1$ degrees of freedom are given in t-tables in most general statistics books, e.g., table 2, page 54, ref. 4.

If CO_2 values lower than about 4 percent (absolute) are to be measured, the number of replicates required becomes large for the standard Orsat with an assumed $\sigma\{\%\text{CO}_2\} = 0.4$ percent as can be seen in figure 6, page 42.

3.2 SUGGESTED PERFORMANCE CRITERIA

Data assessment as discussed in the previous subsection was based on the premise that all variables are controlled at a given level. These levels of suggested performance criteria are the values given in the Operations Manual for determining when equipment and/or personnel variability is out of control. Criteria for judging performance are summarized in table 1.

The criteria for determining the number of analyses to be performed for a field test were arrived at in the following manner. The functional analysis of subsection 4.1 shows that if the standard deviations associated with determining $\%\text{CO}_2$ and $\%\text{O}_2$ are as assumed in the functional analysis, the resulting variability in the mean value determined from three replicates for the dry molecular weight, M_d , can be expressed in terms of a standard deviation as $\sigma\{M_d\} = 0.14$ lb/lb-mole. Three sigma limits for the average of three replicates then are ± 0.42 lb/lb-mole and indicate that a maximum error only slightly larger than 1.5 percent (relative) in M_d should seldom occur when the measurement process is in control (assuming a minimum value of M_d of 29 lb/lb-mole). To control the variability in M_d , it is sufficient to control the measurement variabilities of $\%\text{CO}_2$ and $\%\text{O}_2$. Hence, for a sample size of three (assuming $\sigma\{\%\text{CO}_2\} = \sigma\{\%\text{O}_2\} = 0.4$ percent) the range, R , i.e., the difference in the largest and smallest values of $\%\text{CO}_2$ or $\%\text{O}_2$ should not exceed 1.74 percent (absolute) or 0.87 for a modified Orsat, more than about three times per thousand tests when the process is in control (based on the control chart approach).

When determining the percent by volume of CO_2 in cases where the particulate emissions level of incinerator is to be corrected to 12 percent CO_2 , it is desirable to control the variability as a function of the CO_2 level being measured. Figure 6 shows the number of replicates required to be 98 percent confident that the average of the measured values is within ± 10 percent (relative of the true value as a function of the CO_2 level being measured). These data are given for the standard Orsat (assumed standard deviation of 0.4 percent) and for the modified Orsat (assumed standard deviation of 0.2 percent).

Table 1: SUGGESTED PERFORMANCE CRITERIA

1. Suggested Criteria for Determining the Number of Analyses per Field Test

- a) When the data are to be used for determining M_d only, use the first three consecutive analyses for which the range,

Standard Orsat: $R \leq 1.74$ percent (absolute)

Modified Orsat: $R \leq 0.87$ percent (absolute)

for both CO_2 and O_2 determinations.

- b) For determining percent CO_2 for correcting the particulate emissions level to 12 percent CO_2 , determine the number of replicate analyses, r , from figure 6, page 42, according to the type of Orsat being used. Use the average of the first three analyses as $\%CO_{2t}$.

Also, the range, R , of the r replicates must be no greater than $D_2\sigma$ as shown in the table, i.e., $R \leq D_2\sigma$ for r replicates. (See table 9, page 70, of reference 4 for additional values of D_2 .)

Number of Replicates, r	Multiple of D_2 (for 3σ Values)	$R \leq D_2\sigma$ (Percent)	
		$\sigma = 0.4$ percent	$\sigma = 0.2$ percent
3	4.358	1.74	0.87
4	4.698	1.88	0.94
5	4.918	1.97	0.99
6	5.078	2.03	1.02
7	5.203	2.08	1.04
8	5.307	2.12	1.06
9	5.394	2.16	1.08
10	5.469	2.19	1.10
11	5.534	2.21	1.11

2. Suggested Criteria for Performing a Calibration Check

Perform a calibration check every third field test or after three months, whichever occurs first.

3. Suggested Criteria for Replacing Absorbing Reagent

Replace the applicable absorbing reagent when 10 or more passes are required to reach a constant volume for a component gas.

It must be emphasized that these limits were arrived at from a small quantity of data. They are only suggested as a starting point. After 25 or 30 tests have been performed, the limits should be reevaluated and tightened if possible. The limits should not be relaxed without the approval of the Environmental Protection Agency.

3.3 COLLECTION AND ANALYSIS OF INFORMATION TO IDENTIFY TROUBLE

In a quality assurance program, one of the most effective means of preventing trouble is to respond immediately to indications of suspicious data or equipment malfunctions. There are certain visual and operational checks that can be performed while the measurements are being made to help assure the collection of data of good quality. These checks are written as part of the routine operating procedures in section II. In order to effectively apply preventive-type maintenance procedures to the measurement process, the supervisor must know the important variables in the process, know how to monitor the critical variables, and know how to interpret the data obtained from monitoring operations. These subjects are discussed in the following subsections.

3.3.1 Identification of Important Variables

Determination of stack gas composition requires a sequence of operations and measurements that yields as an end result a number that serves to represent the average molecular weight or average percent of a component gas for that field test. There is no way of knowing the accuracy, i.e., the agreement between the measured and the true value, for a given field test. However, a knowledge of the important variables and their characteristics allows for the application of quality control procedures to control the effect of each variable at a given level during the field test, thus providing a certain degree of confidence in the validity of the final result.

A functional analysis of this method of measuring the molecular weight of stack gases was made to try to identify important components of system error. Also, collaborative tests have been performed to determine the repeatability and reproducibility of the Method (refs. 1 and 2). Results from the collaborative tests are used as overall system error while the individual error components are estimated using engineering judgment in a manner such that their combined variability is consistent with overall system error.

Two of the most important error sources are 1) the inability to maintain a constant pressure throughout the test, i.e., the inability to return the sample to atmospheric pressure before making each volume reading, and 2) volumetric reading errors.

These variables are assumed to be important because a modified Orsat analyzer with a section of the burette marked in 0.1 ml divisions to reduce reading error and a small cross section to increase the spacing between divisions making it easier to attain equal levels of the liquid in the burette and the leveling bottle, thereby maintaining a constant pressure, showed a marked improvement in system precision (ref. 1). The standard deviations associated with the measurements of both CO_2 and O_2 were reduced by one-half or better (with a burette as shown in figure 2) over that obtained with a standard Orsat analyzer. Both of these errors are expected to be random, normal deviates with zero means.

Other components of measurement error are:

- (1) failure to make sufficient passes for complete absorption of a component gas,
- (2) failure to saturate the leveling bottle solution with the sample gases, or failure to maintain a saturated salt solution in the leveling bottle,
- (3) exposure of the sample to ambient air,
- (4) spent absorbing reagent, and
- (5) SO_2 interference with CO_2 determinations.

Since the results of the collaborative tests do not indicate a bias among field teams, and a modified analyzer would probably not significantly reduce their effect, the above five error sources are lumped together as a normally distributed variable with a zero mean and treated as a third component of system error for this analysis. This third component accounts for about 20 percent of the total variability when using a standard Orsat analyzer under these assumptions.

A brief description of the assumptions made and the techniques used in the functional analysis is given in subsection 4.1 of this document. A more comprehensive treatment will be given in the final report for this contract. The source and magnitude of uncertainty for each of the above parameters are discussed below.

3.3.1.1 Sample Pressure - A constant pressure is maintained throughout the test by leveling the liquid in the burette to that in the leveling bottle. Some Orsat analyzers are constructed in such a manner that it is difficult to view the burette and the leveling bottle simultaneously. Some standard analyzer burette scales have 1 ml occupying only 4 mm of the burette length (ref. 1). Under field conditions significant errors can easily result with the standard Orsat analyzer. Level differences of as much as ± 1 to 1.5 mm would be expected under adverse conditions. This difference is equivalent to a volume error of about 0.4 percent (absolute). It is assumed for this

analysis that this is one standard deviation; i.e., on the average 68 percent of the errors due to unequal liquid heights will be less than 0.3 percent by volume. It is further assumed that the modified analyzer with a burette scale such that 1 ml occupies about 11 or 12 mm and the scale has 0.1 ml divisions will reduce the standard deviation by a factor of 3 or to 0.1 percent by volume.

3.3.1.2 Volumetric Reading Error - Burette scales on which the distance between 0.2 ml divisions is of the order of 1 mm are subject to significant reading errors under the best of laboratory conditions. Under typical field conditions, it is felt that 0.2 percent (absolute) is a reasonable standard deviation for reading error. Increasing the distance between divisions and marking the scale in 0.1 ml divisions could possibly reduce this variability by a factor of four resulting in a standard deviation of 0.05 percent by volume.

3.3.1.3 Other Error Sources - To obtain an overall standard deviation of about 0.40, it is necessary that the other sources combined have a standard deviation of 0.173 percent and account for less than one-fourth of the total variability. Control of this component of variability is largely dependent upon the conscientiousness and ability of the operator. It should not be particularly sensitive to the equipment being used.

3.3.2 How to Monitor Important Variables

In general, if the procedures outlined in the Operations Manual are followed, the major sources of random variability will be in control. It is felt, however, that as a means of verification of data quality, as well as a technique for monitoring personnel and equipment variability, two quality control charts should be constructed and maintained as part of the quality assurance program. The quality control charts will provide a basis for action with regard to the measurement process; namely, whether the process is satisfactory and should be left alone, or the process is out of control and action should be taken to find and eliminate the causes of excess variability. In the case of this method in which documented precision data are scarce, the quality control charts can be evaluated after a period of time to determine the range of variation that can be expected under normal operating conditions.

The two recommended quality control charts are:

- (1) a range chart for the analyses performed in the field which should serve as an effective monitor of operator variability and, to a lesser extent, equipment variability, and
- (2) a chart for the differences in measured and known values as obtained from calibration checks to monitor equipment and/or operator variability as well as systematic errors (biases).

Discussions of control charts and instructions for constructing and maintaining them are given in many books on statistics and quality control, such as in refs. 4 and 5.

It is good practice to note directly on control charts the reason for out-of-control conditions, if determined, and the corrective actions taken. It is also good practice to maintain control charts in large size, e.g., 8-1/2 x 11 (inches) or larger and to keep them posted on a wall for viewing by all concerned, rather than have them filed in a notebook.

3.3.2.1 Range Chart - Figure 4 is a sample control chart for the range. The chart was constructed for a sample size of three; i.e., only three replicates per field test are used. It is recommended here that the range be computed for the first three analyses performed for a given field test.

A standard deviation of 0.4 percent for the measurement error was assumed in computing $\bar{R}$ and UCL. (For small sample sizes ($r \leq 6$) the lower control limit (LCL) is effectively zero and is not given here.) It is suggested that the same limits be used for both CO₂ and O₂ analyses until sufficient field data are available to calculate $\bar{R}$ and UCL applicable to each component gas and to individual field teams.

The R values are plotted sequentially as they are obtained and connected to the previously plotted point with a straight line. Corrective action, such as instruction in proper operating technique and/or equipment calibration check, should be taken any time one of the following criteria is exceeded:

- (1) One point falls outside the UCL.
- (2) Two out of three consecutive points fall in the warning zone (between 2 σ and 3 σ limits).
- (3) Seven consecutive points fall above the $\bar{R}$ line.

Exceeding any one of the criteria will usually indicate poor technique or equipment malfunction between analyses.

3.3.2.2 Difference Chart - A sample quality control chart for the difference between measured and known values is shown in figure 5. The chart was constructed using a standard deviation of 0.4 percent for the measurement error and assuming that the test gas concentrations are accurately enough known not to substantially increase this variability. Also, it was assumed that there were no biases in the measurements; hence, CL = 0. It is suggested that the chart as set up in figure 5 be used for both CO₂ and O₂ checks until sufficient field data are available to compute new limits.

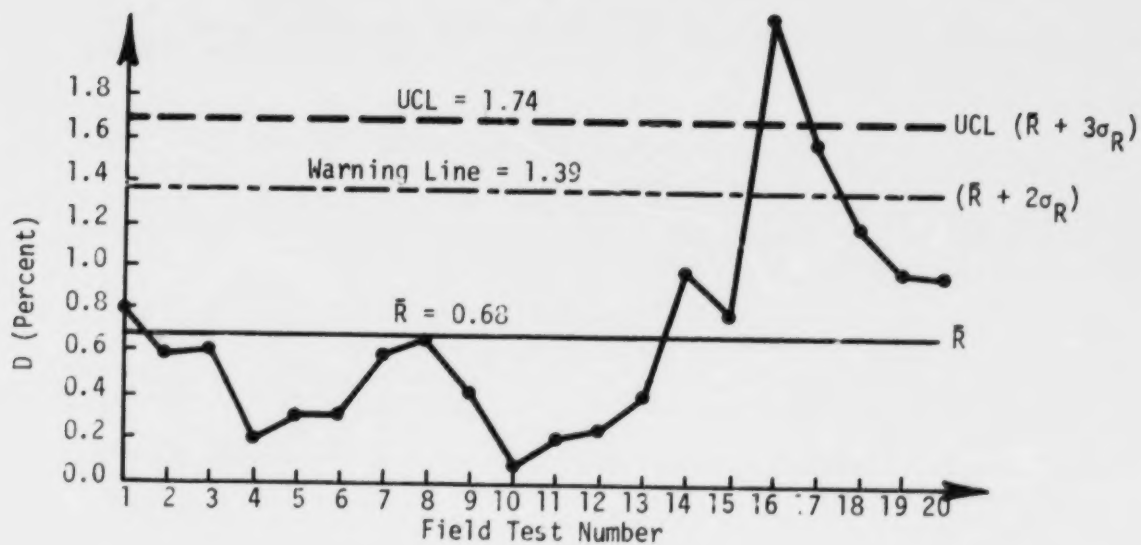


Figure 4: Sample Control Chart for the Range, R , of Field Analyses

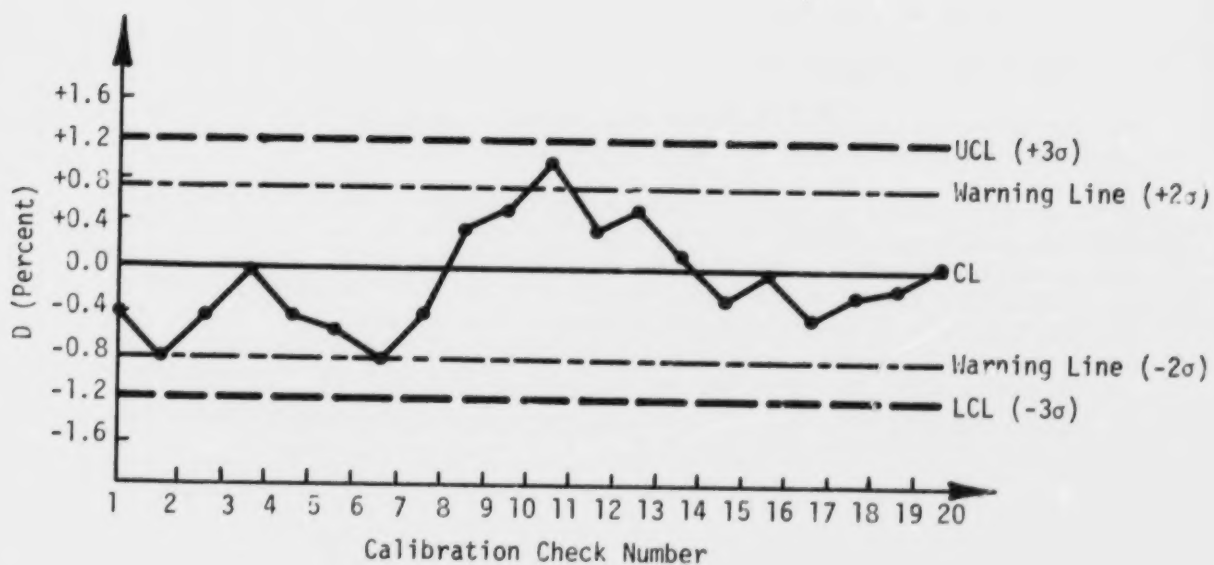


Figure 5: Sample Control Chart for Calibration Checks

For each calibration check, compute

$$D = X_m - X_t$$

where D = The difference in the measured and known concentrations of CO_2 (O_2) in percent,

X_m = The measured concentration of CO_2 (O_2) in percent based on the average of three determinations, and

X_t = The true or known concentration of CO_2 (O_2) in the calibration gas in percent.

Plot each D value on the quality control chart as it is obtained and connect it to the previously plotted point with a straight line.

Corrective action such as replacing the absorbing reagent, performing other equipment repair, and/or providing instructions on proper operating procedures should be taken any time one of the following criteria is exceeded:

- (1) One point falls outside the region between the lower and upper control limits.
- (2) Two out of three consecutive points fall in the warning zone, i.e., between the 2σ and 3σ limits.
- (3) Seven consecutive points fall on the same side of the center line.

Exceeding the first and second criteria will usually indicate poor technique or equipment malfunction. The third criterion when exceeded indicates a system bias due either to a faulty analyzer or a consistent error in performing operating procedures.

SECTION IV

MANUAL FOR MANAGER OF GROUPS OF FIELD TEAMS

4.0 GENERAL

The guidelines for managing quality assurance programs for use with Test Method 3 - Gas Analysis for Carbon Dioxide, Excess Air, and Dry Molecular Weight are given in this part of the field document. This information is written for the manager of several teams for measuring source emissions and for the appropriate EPA, State, or Federal Administrators of these programs. It is emphasized that if the analyst carefully adheres to the operational procedures and checks of section II, then the errors and/or variations in the measured values should be consistent with the performance criteria as suggested. Consequently, the auditing routines given in this section provide a means of determining whether the stack sampling test teams of several organization, agencies, or companies are following the suggested procedures. The audit function is primarily one of independently obtaining measurements and performing calculations where this can be done. The purpose of these guidelines is to:

- (1) present information relative to the test method (a functional analysis) to identify the important operations and factors,
- (2) present a data quality audit procedure for use in checking adherence to test methods and validating that performance criteria are being satisfied, and
- (3) present the statistical properties of the auditing procedure in order that the appropriate plan of action may be selected to yield an acceptable level of risk to be associated with the reported results.

These three purposes will be discussed in the order stated in the sections that follow. The first section will contain a functional analysis of the test method with the objective of identifying the most important factors that affect the quality of the reported data and of estimating the expected variation and bias in the measurements resulting from equipment and operator errors.

There are no absolute standards with which to compare the routinely derived measurements. Furthermore, the taking of completely independent measurements at the same time that the routine data are being collected (e.g., by introducing two pitot tubes into the stack and collecting two samples simultaneously) is not considered practical due to the constrained environmental and space conditions under which the data are being collected. Hence, a combination of an on-site system audit, including visual observation of adherence to operating procedures and a quantitative performance quality audit check, is recommended as a dual means of independently checking on the source emissions data.

The second section contains a description of a data quality audit procedure. The most important variables identified in section 4.1 are considered in the audit. The procedure involves the random sampling of n stacks from a lot size of $N = 20$ stacks (or from the stacks to be tested during a 3-month period, if less than 20) for which one firm is conducting the source emissions tests. For each of the stacks selected, independent measurements will be made of the indicated variables. These measurements will be used in conjunction with the routinely collected data to estimate the quality of the data being collected by the field teams.

The data quality audit procedure is an independent check of data collection and analysis techniques with respect to the important variables. It provides a means of assessing data collected by several teams and/or firms with the potential of identifying biases/excessive variation in the data collection procedures. A quality audit should not only provide an independent quality check, but also identify the weak points in the measurement process. Thus the auditor, an individual chosen for his background knowledge of the measurement process, will be able to guide field teams in using improved techniques. In addition, the auditor is in a position to identify those procedures employed by some field teams that are improvements over the current suggested ones, either in terms of data quality and/or time and cost of performance. The auditor's role will thus be one of aiding the quality control function for all field teams for which he is responsible, utilizing the cross-fertilization of good measurement techniques to improve the quality of the collected and reported data.

The statistical sampling and test procedure recommended is sampling by variables. This procedure is described in section 4.3. It makes maximum use of the data collected, and it is particularly adaptable to the small lot size and consequently the small sample size applications. The same sampling plans can be employed in the quality checks performed by a team or firm in its own operations. The objectives of the sampling and test procedure are to characterize data quality for the user and to identify potential sources of trouble in the data collection process for the purpose of correcting the deficiencies in data quality.

4.1 FUNCTIONAL ANALYSIS OF TEST METHOD

Test Method 3 - Gas Analysis for Carbon Dioxide, Excess Air, and Dry Molecular Weight is described in the Federal Register of December 23, 1971 and reproduced as appendix A of this document. Under standards of performance for new stationary sources, Method 3 is used to determine the dry molecular weight of the stack gas by measuring the percent by volume of CO_2 and O_2 in the gas. Also, when testing for particulate emissions of incinerators, the measured CO_2 is used to correct the emissions level to 12 percent CO_2 . The functional analysis addresses itself only to the determination of molecular weight and to the special case where particulate

emissions are to be corrected to 12 percent CO_2 in which case a higher accuracy in the CO_2 determination is desired.

The dry molecular weight is given by

$$M_d = 0.44 (\overline{\% \text{CO}_2}) + 0.32 (\overline{\% \text{O}_2}) + 0.28 (\% \text{N}_2 + \% \text{CO}) \quad (1)$$

where M_d = Dry molecular weight, lb/lb-mole,

$\overline{\% \text{CO}_2}$ = Average percent carbon dioxide by volume from at least three analyses, dry basis,

$\overline{\% \text{O}_2}$ = Average percent oxygen by volume from at least three analyses, dry basis, and

$(\% \text{N}_2 + \% \text{CO}) = 100 - \overline{\% \text{CO}_2} - \overline{\% \text{O}_2}$, dry basis.

The percent carbon dioxide by volume is determined by the average of at least three analyses. The effect of errors in the analyses of the individual components to the errors in estimating true dry molecular weight, M_{dt} , and the true percent CO_2 by volume, $\% \text{CO}_{2t}$, are discussed in the following subsections.

4.1.1 Variance Analysis

The standard deviations of the percent carbon dioxide and percent oxygen by volume as obtained by the Orsat analysis are both assumed to be 0.4 percent by volume, i.e., $\sigma\{\% \text{CO}_2\} = \sigma\{\% \text{O}_2\} = 0.4$ percent (absolute) when using a standard Orsat analyzer, and $\sigma\{\% \text{CO}_2\} = \sigma\{\% \text{O}_2\} = 0.2$ percent (absolute) when using a modified Orsat analyzer as shown in figure 2 of section II. The values used for the modified analyzer are of the order of those obtained from a collaborative test using such an analyzer (ref. 1). Standard deviations of 0.38 percent and 0.82 were obtained for determinations of CO_2 and O_2 , respectively, from a collaborative test using a standard Orsat analyzer (ref. 2). Although the variability in measuring O_2 was much larger than that for measuring CO_2 using the standard Orsat analyzer, it was somewhat less than using the modified Orsat analyzer. For this analysis, the standard deviation for determining CO_2 as obtained from the collaborative tests is used for both component gases.

Briefly, for the standard Orsat analyzer, the following assumptions were made for single measurements of either CO_2 or O_2 ,

$$\sigma^2(\%CO_2) = \sigma^2(\%O_2) = \sigma_P^2 + \sigma_R^2 + \sigma_O^2$$

and $\sigma^2(\%CO_2) = 0.16$, $\sigma_P^2 = 0.09$, $\sigma_R^2 = 0.04$, and $\sigma_O^2 = 0.03$,

where σ_P = Variability in returning the sample to and maintaining atmospheric pressure when making volume readings (ability to attain equal levels of the liquid in the burette and the leveling bottle),

σ_R = Reading error judged to be 0.2 percent for the standard Orsat.

σ_O = All other error sources combined.

If these assumptions are reasonable, then reading and pressure errors account for about 80 percent of the total variability. Furthermore, if the modified analyzer as shown in figure 2, page 9, accomplishes the following

$$\sigma^2(\%O_2) = \sigma^2(\%CO_2) = 0.04, \sigma_P^2 = 0.0075, \sigma_R^2 = 0.0025, \text{ and } \sigma_O^2 = 0.03,$$

then the reading and pressure errors account for only 25 percent of the total variability leaving other error sources to account for 75 percent of the variability. For further improvement on precision, actions should be taken to identify and control sources of variations within this group called "other error sources."

Further background concerning the assumptions made in the analyses and the methodology of this section will be contained in the final report of this contract.

4.1.1.1 Analysis of M_d - Referring to equation (1) for dry molecular weight, the following equation is determined to relate the variances of the measurements, under the assumption that the errors in measuring percent CO_2 and O_2 are uncorrelated.

$$\sigma^2(M_d) = (0.44)^2 \sigma^2(\overline{\%CO_2}) + (0.32)^2 \sigma^2(\overline{\%O_2}) + (0.28)^2 \sigma^2(\overline{\%N_2} + \overline{\%CO}). \quad (2)$$

The above assumption is conservative since reading errors have a negative correlation of -0.5 which would result in a smaller value of $\sigma\{M_d\}$.

Errors due to incomplete absorption of CO_2 , then subsequent absorption when determining O_2 , would also have a negative correlation. Therefore, this is a worst case approach.

The variance of the average of r replications of percent CO_2 by volume is

$$\sigma^2\{\overline{XCO_2}\} = \frac{\sigma^2\{XCO_2\}}{r} = \frac{(0.4)^2}{r}$$

Assuming a minimum of three (3) replications and that all the variances are equal to $(0.4)^2$, then equation (2) becomes

$$\sigma^2\{M_d\} = (0.4)^2 \cdot 0.3744/3 = 0.02$$

or

$$\sigma\{M_d\} = 0.14 \text{ lb/lb-mole.}$$

The coefficient of variation of M_d is $CV\{M_d\} = 100 \times \sigma\{\bar{M}_d\}/\bar{M}_{dt}$, where $\bar{M}_{dt}$ is the true mean value. Thus, if $\bar{M}_{dt} = 30.0$ lb/lb-mole, the coefficient variation is about 0.5 percent based on an average of three replicates. Hence, it is expected that the $\bar{M}_d$ based on the average of three determinations on each component using a standard Orsat will be estimated with precision within 0.42 lb/lb-mole (3σ limits).

It should also be noted that the true value of M_d should fall between 29 and 31.3 lb/lb-mole, and that if the average value 30.15 were used (independently of any measured values), the maximum error would be 1.15 lb/lb-mole, or the maximum relative error would be $1.15/29 = 0.04$ or 4 percent compared to 0.5 percent for measured M_d based on the average of three replicates. Because M_d appears as $\sqrt{M_d}$ in equations for the determination of emissions, the relative error in the final determination would be 2 percent, indicating that for practical consideration the errors in estimating M_d are not critical unless the final answer is to be determined to a finer precision than the 2 percent value.

4.1.1.2 Analysis of $\%CO_2$ by Volume - A more critical measurement is the $\%CO_2$ when it is used to correct the emissions level to 12 percent CO_2 for estimating the particulate emissions of incinerators. In the special case where a high degree of precision is desired for the CO_2 determination, the required number of replicate analyses is computed as follows on the basis that the measurements of $\%CO_2$ are normally distributed about a true mean, $\overline{\%CO_{2t}}$, and with a standard deviation of $\sigma\{\%CO_2\} = 0.4$ percent by volume. Using the fact that the mean of r replications is also normally distributed (this assumption is reasonable even if the original individual measurements were not normally distributed) about the same true mean (assuming no bias) with a standard deviation of

$$\sigma\{\overline{\%CO_2}\} = 0.4/\sqrt{r},$$

then the probability that the absolute deviation between the measured mean and the true mean is less than a positive number ϵ is given by

$$P\{|\overline{\%CO_2} - \overline{\%CO_{2t}}| < \epsilon\} = 2\phi\left(\frac{\epsilon}{\sigma}\right) - 1, \quad (3)$$

where $\sigma = 0.4/\sqrt{r}$, and $\phi\left(\frac{\epsilon}{\sigma}\right)$ is the area under the standard normal curve to the left of the value $x = \epsilon/\sigma$. This value is tabulated in the standard tables, e.g., see ref. 6. Now suppose that it is desired that ϵ be $0.10 (\%CO_{2t})$, 10 percent of the true mean, and that the probability be 0.98. That is, 98 percent of the time the average of r measured values will be within ± 10 percent of the true CO_2 concentration.

Under these conditions, $\frac{\epsilon}{\sigma} \approx 2.33$, the 99th percentile of the standard normal variable, in order that $2\phi(2.33) - 1 = 2(0.99) - 1 = 0.98$. Thus,

$$\frac{\epsilon}{\sigma} = \frac{0.10 (\%CO_{2t})}{0.4/\sqrt{r}} = 2.33$$

and

$$r \approx \frac{87}{\left(\overline{\%CO_{2t}}\right)^2}. \quad (4)$$

The required number of replicates r , for the desired precision is given in figure 6 as a function of $\overline{\%CO_{2t}}$ for both standard and modified Orsats with assumed standard deviations of 0.4 and 0.2 lb/lb-mole, respectively. A

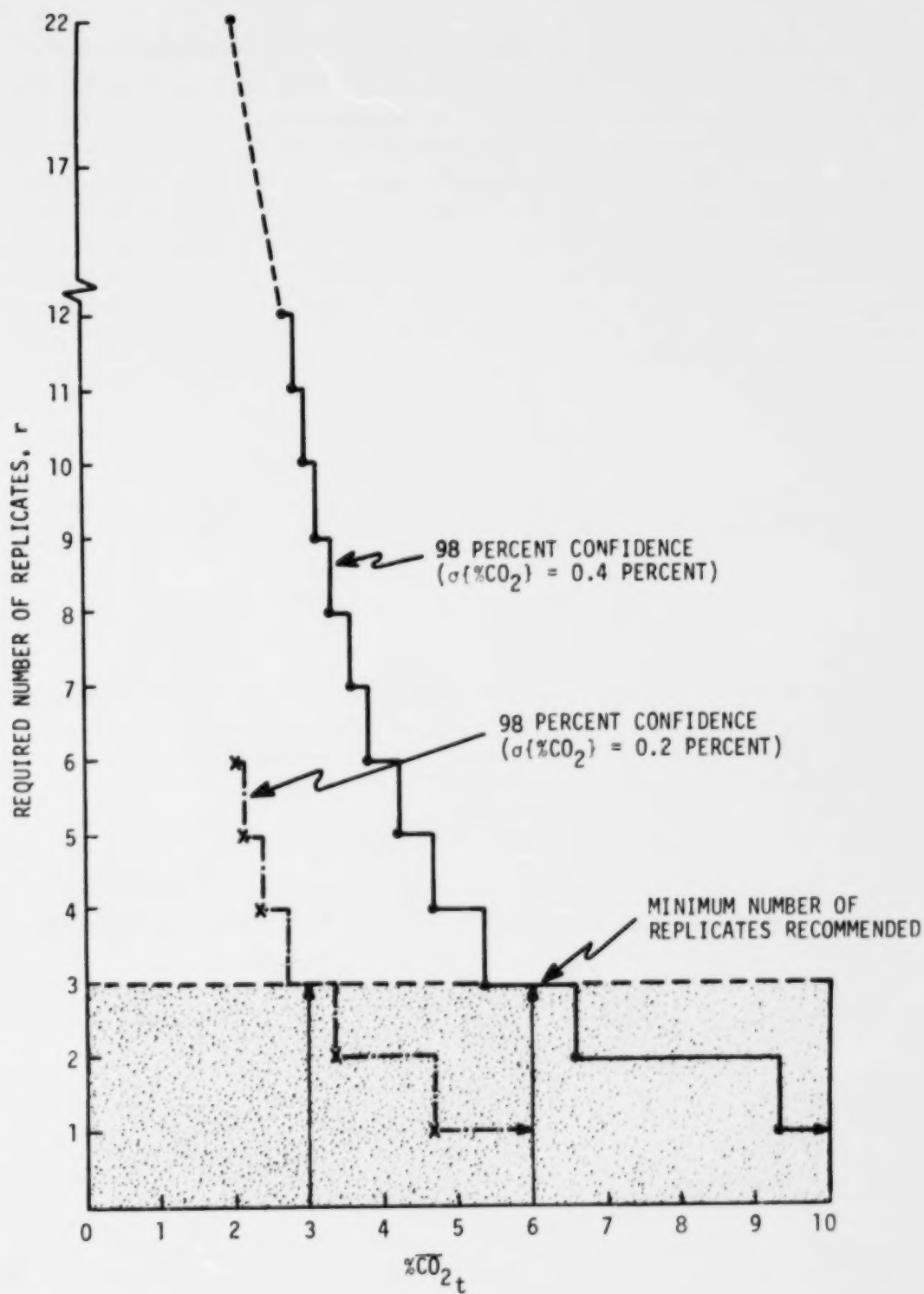


Figure 6: Number of Replications r for Estimating $\%CO_{2t}$ to Within ± 10 Percent with 98 Percent Confidence.

minimum of three replicates is recommended under all conditions. Also, the average of three replicates is recommended to estimate $\overline{\%CO_2}_t$ to determine r .

From figure 6 it can be seen that three replicates are sufficient for any $\overline{\%CO_2}_t$ levels greater than 3 percent (absolute) when the replicability is 0.2 percent (absolute) or less. Three replicates are adequate for $\overline{\%CO_2}_t$ levels greater than about 6 percent (absolute) when the replicability as expressed by a standard deviation is no greater than 0.4 percent (absolute).

4.1.1.3 Control Chart for the Range, R, of Replicate Analyses - The above results depend directly on the assumption that $\sigma\{\%CO_2\} = 0.4\%$ or 0.2% by volume for any CO_2 level. This assumption can be checked on a continuous basis using the range, R, of the replicate analyses and comparing against the expected variation in the range as given by a standard control chart as recommended in subsection 3.3.2.1. The range of r replicates is defined as the largest value less the smallest value. The $+3\sigma$ limit, i.e., the UCL is given in table 1, page 29, for $r = 3$ through 11, and for assumed standard deviations of 0.4 percent and 0.2 percent.

For r larger than 6, it is suggested that the measurements be subdivided into groups of nearly equal size between 3 and 6, as is possible. If a constant $r = 3$ can be used, then the points (ranges) can be plotted on a control chart with upper limit 1.74, which should be exceeded only about 3 times in 1000 for $\sigma = 0.4$ percent by volume. Such a control chart is illustrated in figure 4, page 34.

4.1.2 Bias Analysis

The bias analyses of the two measures of interest, M_d and $\%CO_2$, are straightforward. Suppose that there is a bias in the measurement of the percent carbon dioxide by volume due to faulty equipment or a consistent error in performing the operating procedures. The average of r replications of the measurement will also be biased by the same amount. Denote the biases in $\%CO_2$ (or $\overline{\%CO_2}$) and $\%O_2$ by τ_{CO_2} and τ_{O_2} , respectively. Then the bias in $100 - \%CO_2 - \%O_2$ would be $-\tau_{CO_2} - \tau_{O_2}$. Substituting the biases for each component into equation (1) yields the corresponding bias in M_d , that is,

$$\begin{aligned}\tau_{M_d} &= 0.44 \tau_{CO_2} + 0.32 \tau_{O_2} + 0.28 (-\tau_{CO_2} - \tau_{O_2}) \\ \tau_{M_d} &= 0.16 \tau_{CO_2} + 0.04 \tau_{O_2} .\end{aligned}\tag{5}$$

Hence, the bias in M_d is relatively small compared to the biases in the individual component because of the offsetting or cancellation effect. These biases are estimated as described in section 4.3.1.

4.2 PROCEDURES FOR PERFORMING A QUALITY AUDIT

"Quality audit" as used here implies a comprehensive system of planned and periodic audits to verify compliance with all aspects of the quality assurance program. Results from the quality audit provide an independent assessment of data quality. "Independent" means that the individuals performing, and as much as possible of the equipment used in the audit, are different from the regular field crew and equipment. From these data both bias and precision estimates can be made for the analysis phase of the measurement process.

The auditor, i.e., the individual performing the audit, should have extensive background experience in source sampling, specifically with the characterization technique that he is auditing. He should be able to establish and maintain good rapport with field crews.

The functions of the auditor are summarized in the following list:

- (1) Observe procedures and techniques of the field team during on-site measurements.
- (2) Analyze a split sample on-site using own analyzer.
- (3) Check/verify applicable records of equipment calibration checks and quality control charts in the field team's home laboratory.
- (4) Perform calculations using data obtained from the audit.
- (5) Compare the audit value with the field team's test value.
- (6) Inform the field team of the comparison results specifying any area(s) that need special attention or improvement.
- (7) File the records and forward the comparison results with appropriate comments to the manager.

4.2.1 Frequency of Audit

The optimum frequency of audit is a function of certain costs and desired level of confidence in the data quality assessment. A methodology for determining the optimum frequency using relevant costs is presented in the Quality Assurance Documents for the methods requiring the results of Method 3 and in the final report for this contract. Costs will vary among

field teams and types of field tests. Therefore, the most cost effective auditing level will have to be derived using relevant local cost data according to the procedure given in the final report on this contract. Since the potential error is much greater for particulate emissions of incinerators, cost considerations may indicate that only incinerator tests should be audited.

4.2.2 Collecting On-Site Information

While on-site, the auditor should observe the field team's overall performance of the field test. Specific operations to observe should include, but not be limited to:

- (1) Setting up and leak testing the sampling train.
- (2) Purging the sampling train with stack gas prior to collecting the sample.
- (3) Proportional sampling.
- (4) Transfer of sample from the collapsible bag to the Orsat analyzer.

The above observations, plus any others that the auditor feels are important, can be used in combination to make an overall evaluation of the team's proficiency in carrying out this portion of the field test.

In addition to the above on-site observations, it is recommended that the auditor have his personal Orsat analyzer, preferably a modified one, and perform analyses of the gas at the same time that the field team is performing its analyses. The auditor should perform the analyses according to the procedures given in section II.

4.2.2.1 Comparing Audit and Routine Values of M_d - In field tests

requiring only the molecular weight, the audit and routine (field team's results) values are compared by

$$d_j = M_{d_j} - M_{da_j}$$

where d_j = The difference in the audit and field test results for the j^{th} audit, lb/lb-mole,

M_{da_j} = Audit value of dry molecular weight, lb/lb-mole, and

M_{d_j} = Dry molecular weight obtained by the field team, lb/lb-mole.

Record the value of d_j in the quality audit log book.

4.2.2.2 Comparing Audit and Routine Values of CO₂ - When testing an incinerator for particulate emissions (Method 5), in addition to calculating d_j as described above, it is necessary to compare audited and routinely derived values for CO₂ by calculating

$$D_j = \overline{\%CO_2}_j - \overline{\%CO_2}_{a_j}$$

where D_j = The difference in the audit and field test results for the j^{th} audit, percent,

$\overline{\%CO_2}_{a_j}$ = Audit value of %CO₂ as the average of r replicates, percent, and

$\overline{\%CO_2}_j$ = Field team's value of %CO₂ as the average of r replicates, percent.

Record the value of D_j in the quality audit log book.

4.2.3 Collecting Laboratory Information

When visiting the field team's home laboratory, the auditor should verify by checking the records that the performance criteria as given in 1 of section II have been met over the period since the last audit was performed.

4.2.4 Overall Evaluation of Field Team Performance

In a summary-type statement the field team should be evaluated on its overall performance. Reporting the d_j value and, when applicable, the D_j value as previously computed, is an adequate representation of the objective information collected for the audit. However, unmeasurable errors can result from nonadherence to the prescribed operating procedures and/or from poor technique in executing the procedures. These error sources have to be estimated subjectively by the auditor. Using the notes taken in the field, the team could be rated on a scale of 1 to 5 as follows:

- 5 - Excellent
- 4 - Above average
- 3 - Average
- 2 - Acceptable, but below average
- 1 - Unacceptable performance.

In conjunction with the numerical rating, the auditor should include justification for the rating. This could be in the form of a list of the team's strong/weak points.

4.3 DATA QUALITY ASSESSMENT

Two aspects of data quality assessment are considered in this section. The first considers a means of estimating the precision and accuracy of the reported data, e.g., reporting the bias, if any, and the standard deviation associated with the measurements. The second consideration is that of testing the data quality against given standards using sampling by variables. For example, lower and upper limits, L and U, may be selected to include a large percentage of the measurements and outside of which it is desired to control the percentage of measurements to, say, less than 10 percent. If the data quality is not consistent with these limits, L and U, then action is taken to correct the possible deficiency before future field tests are performed and to correct the previous data when possible.

4.3.1 Estimating the Precision/Accuracy of the Reported Data

Methods for estimating the precision (standard deviation) and accuracy (bias) of the dry molecular weight measurements and the percent CO₂ by volume were given in section 4.1. This section will indicate how the audit data collected in accordance with the procedure described in section 4.2 will be utilized to estimate the precision and accuracy of the two measures of interest. Similar techniques can also be used by a specific firm or team to assess their own measurements. However, in this case no bias data among firms can be obtained. Two sets of audit data will be collected as a result of following the procedures in the previous section. They are:

$$d_j = M_{d_j} - M_{da_j}$$

and

$$D_j = \overline{\%CO_2}_j - \overline{\%CO_2}_{a_j}.$$

In practice, it may be decided to collect data on D_j only in pertinent circumstances because the errors in the determinations of M_d are small. These are differences between the field team results and the audited results for the respective measurements. Let the means and standard deviations of the differences d_j and D_j $j=1, \dots, n$ be denoted by $\bar{d}$, s_d and $\bar{D}$, S_D , respectively.

Thus

$$\bar{d} = \sum_{j=1}^n d_j / n,$$

and

$$s_d = \left[\sum_{j=1}^n (d_j - \bar{d})^2 / (n - 1) \right]^{1/2}$$

Identical formulas replacing D for d are obtained for D and s_D , respectively. Now $\bar{d}$ and $\bar{D}$ are estimates of the biases in the measurements (i.e., relative to the audited value). Assuming the audited data to be unbiased, the existence of a bias in the field data can be checked by the appropriate t-test, i.e.,

$$t = \frac{\bar{d} - 0}{s_d / \sqrt{n}} .$$

See ref. 7 for a discussion of the t-test.

If t is significantly large, say greater than the tabulated value of t with n - 1 degrees of freedom, which is exceeded by chance only 5 percent of the time, then the bias is considered to be real and some check should be made for a possible cause of the bias. If t is not significantly large, then the bias should be considered zero and the accuracy of the data is acceptable.

The standard deviation s_d (or s_D) is a function of both the standard deviation of the field measurements and of the audit measurements. Assuming both the field and audited measurements are obtained using the same type of Orsat analyzer and hence that the standard deviations are expected to be the same, then s_d is an estimate of $\sqrt{2} \sigma(M_d) \sqrt{r}$, where r is the number of replications. Table 2, page 51, contains an example calculation of $\bar{d}$ and s_d starting with the differences for a sample size of n = 7. See the final report on the contract for further information concerning this result.

Similarly, s_D is an estimate of

$$\sqrt{2} \sigma(\overline{XCO}_2) = \frac{\sqrt{2} \sigma(XCO_2)}{\sqrt{r}} .$$

These standard deviations can then be utilized to check the reasonableness of the assumptions made in section 4.1 concerning $\sigma(XCO_2) = \sigma(XO_2) = 0.4$ percent (or 0.2 percent for the modified Orsat analyzer), and $\sigma(M_d) = 0.14$ lb/lb-mole. For example, the estimated standard deviation, s, may be directly

checked against the assumed value, σ , by using the statistical test procedure

$$\frac{\chi^2}{f} = \frac{s^2}{\sigma^2},$$

where χ^2/f is the value of a random variable having the chi-square distribution with $f = n - 1$ degrees of freedom. If χ^2/f is larger than the tabulated value exceeded only 5 percent of the time, then it would be concluded that the test procedure is yielding more variable results due to faulty equipment or operational procedure. The values of s_d and s_D can be used directly in the test given above, if σ^2 is replaced by $2\sigma^2$, on the assumption that the variance of the field measurements is equal to that for the audited data. Thus,

$$\frac{\chi^2}{f} = \frac{s_d^2}{2\sigma^2\{\%CO_2\}/r} \text{ or } \frac{s_D^2}{2\sigma^2\{M_d\}/r}.$$

The measured values should be reported along with the estimated biases, standard deviations, the number of audits, n , and the total number of field tests, N , sampled ($n \leq N$). Estimates, i.e., s_d , s_D , $\bar{d}$, or $\bar{D}$, that are significantly different from the assumed population parameters should be identified on the data sheet. For example, for M_d , based on the data of table 2, the results would be reported as $M_d = 30.4$ (assumed), $t_{M_d} = -0.2$ lb/lb-mole, $s_d/\sqrt{2} = 0.406/\sqrt{2} = 0.29$ lb/lb-mole, $n = 7$, and $N = 20$.

The t-test and χ^2 -test described above, and in further detail in the final report on this contract, are used to check on the biases and standard deviations separately. In order to check on the overall data quality as measured by the percent of measurement deviations outside prescribed limits, it is necessary to use the approach described in subsection 4.3.2 below.

4.3.2 Sampling by Variables

Because the lot size (i.e., the number of field tests performed by a team or laboratory during a particular time period, normally a calendar quarter) is small, $N = 20$, and, consequently, the sample size is small, of the order of $n = 3$ to 8, it is important to consider a sampling by variables approach to assess the data quality with respect to prescribed limits. That is, it is desired to make as much use of the data as possible. In the variables approach, the means and standard deviations of the sample of n audits are used in making a decision concerning the data quality.

Some background concerning the assumptions and the methodology is repeated below for convenience. However, one is referred to one of a number of publications having information on sampling by variables; e.g., see refs. 8-13. The discussion below will be given in regard to the specific problem herein which has some unique features as compared with the usual variable sampling plans.

In the following discussion it is assumed that only %CO₂ and M_d are audited as directed in sections 4.2.2.1 and 4.2.2.2.

The difference between the team-measured and audited value of M_d is designated as d_j, and the mean difference over n audits by $\bar{d}$, that is,

$$\bar{d} = \frac{\sum_{j=1}^n (M_{d_j} - M_{da_j})}{n} .$$

Theoretically, M_d and M_{da} should be measures of the same molecular weight, and their difference should have a mean of zero on the average. In addition, this difference should have a standard deviation equal to $\sqrt{2}$ times that associated with measurements of M_d or M_{da}. Recall from the variance analysis that the difference of two such measurements would have a standard deviation equal to $\sqrt{2} \times 0.14$ lb/lb-mole (based on the average of 3 replicates).

Assuming three standard deviation limits, the values $-3(0.14\sqrt{2})$ and $3(0.14\sqrt{2})$ lb/lb-mole define lower and upper limits, L and U, respectively, outside of which it is desired to control the proportion of differences, d_j. Following the method given in ref. 11, a procedure for applying the variables sampling plan is described below. Figures 7 and 8 illustrate examples of satisfactory and unsatisfactory data quality with respect to the prescribed limits L and U.

The variables sampling plan requires the sample mean difference, $\bar{d}$; the standard deviation of these differences, s_d; and a constant, k, which is determined by the value of p, the proportion of the differences outside the limits of L and U. For example, if it is desired to control at 0.10, the probability of not detecting lots with data quality p equal to 0.20 (or 20% of the individual differences outside L and U) and if the sample size n = 7, then the value of k can be obtained from table II of ref. 11. The values of $\bar{d}$ and s_d are computed in the usual manner; see table 2

Table 2. COMPUTATION OF MEAN DIFFERENCE, $\bar{d}$, AND
STANDARD DEVIATION OF DIFFERENCES, s_d

General Formulas		Specific Example	
$d = M_{dj} - M_{da_j}$		Data (lb/lb-mole)	
d_1	d_1^2	0.4	0.16
d_2	d_2^2	-0.2	0.04
d_3	d_3^2	0.1	0.01
d_4	d_4^2	-0.8	0.64
d_5	d_5^2	-0.6	0.36
d_6	d_6^2	-0.3	0.09
d_7	d_7^2	-0.1	0.01
Σd_j	Σd_j^2	-1.5,	1.31
$\bar{d} = \frac{\Sigma d_j}{n}$		$\bar{d} = -0.214$	
$s_d^2 = \frac{\Sigma d_j^2 - \frac{(\Sigma d_j)^2}{n}}{(n-1)}$		$s_d^2 = 0.165$	
$s_d = \sqrt{s_d^2}$		$s_d = 0.406$	

Table 3. SAMPLE PLAN CONSTANTS, k for $P\{\text{not detecting a lot with proportion } p \text{ outside limits } L \text{ and } U\} \leq 0.1$

Sample Size n	$p = 0.2$	$p = 0.1$
3	3.039	4.258
5	1.976	2.742
7	1.721	2.334
10	1.595	2.112
12	1.550	2.045

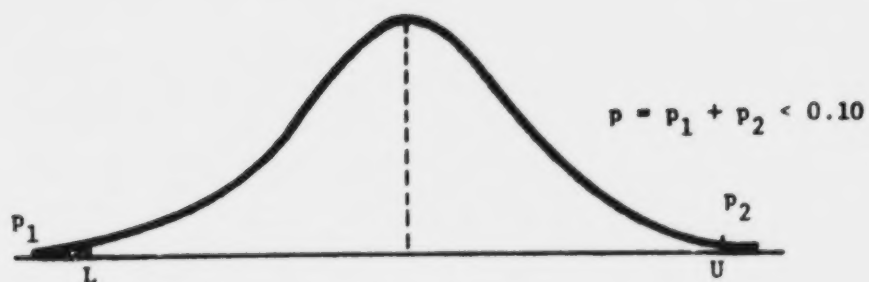


Figure 7. Example Illustrating $p < 0.10$ and Satisfactory Data Quality.

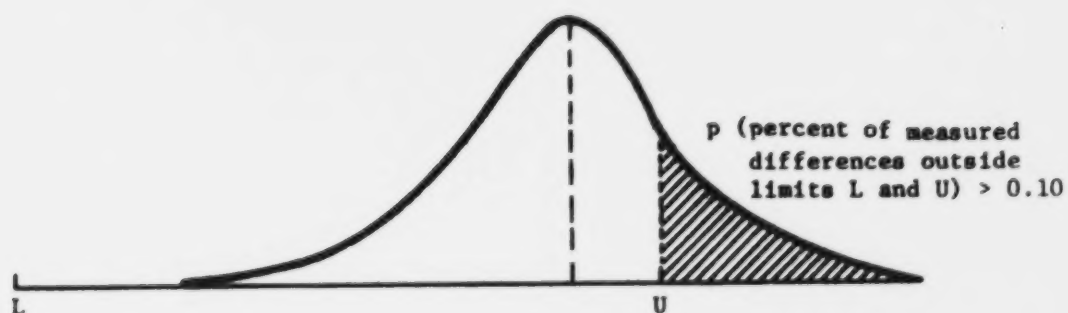


Figure 8. Example Illustrating $p > 0.10$ and Unsatisfactory Data Quality.

for formulas and a specific example. Given the above information, the test procedure is applied, and subsequent action is taken in accordance with the following criteria:

- (1) If both of the following conditions are satisfied:

$$\bar{d} - k s_d \geq L = -0.42\sqrt{2} = -0.597 \text{ lb/lb-mole}$$

$$\bar{d} + k s_d \leq U = 0.42\sqrt{2} = +0.597 \text{ lb/lb-mole.}$$

the individual differences are considered to be consistent with the prescribed data quality limits and no corrective action is required.

- (2) If one or both of these inequalities is violated, possible deficiencies exist in the measurement process as carried out for that particular lot (group) of field tests. These deficiencies should be identified and corrected before future field tests are performed. Data corrections should be made when possible, i.e., if a quantitative basis is determined for correction.

Table 3 contains a few selected values of n , p , and k for convenient reference.

Using the values of $\bar{d}$ and s_d in table 2, $k = 1.721$ for a sample size $n = 7$, and $p = 0.20$, the test criteria can be checked; i.e.,

$$\bar{d} - k s_d = -0.214 - 0.698 = -0.913 < L = -0.597$$

$$\bar{d} + k s_d = -0.214 + 0.698 = 0.484 < U = 0.597.$$

Therefore, both conditions are not satisfied--specifically the lower limit L was exceeded--and the lot of $N = 20$ measurements is not consistent with the prescribed quality limits. The plan protects one from not detecting lots with 20 percent or more defects (deviations falling outside the designated limits L and U) with a risk of 0.10.

The procedure for auditing the differences, D_j , is identical to the above with D_j substituted for d_j throughout, the standard deviation of D_j .

$\sqrt{2} \times 0.4 \text{ \%CO}_2$ by volume, is substituted for $\sqrt{2} \times 0.14 \text{ lb/lb-mole}$, and L and U become

$$\begin{Bmatrix} L \\ U \end{Bmatrix} = \begin{Bmatrix} - \\ + \end{Bmatrix} 3\sqrt{2} \times \frac{0.4}{\sqrt{r}} \text{ \%CO}_2 \text{ by volume,}$$

where r is the number of replications. The above audit checks assume that the audit and the field measurements are both determined with the standard Orsat analyzer. If the audit is performed using the modified Orsat analyzer, the audit data would be more precise and the results of the above tests would also have to be modified. The final report on this contract will consider these variations in the test procedure.

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APPENDIX A

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RULES AND REGULATIONS

METHOD 3—GAS ANALYSIS FOR CARBON DIOXIDE, EXCESS AIR, AND DRY MOLECULAR WEIGHT

1. Principle and applicability

1.1 Principle. An integrated or grab gas sample is extracted from a sampling point and analyzed for its components using an Orsat analyzer.

1.2 Applicability. This method should be applied only when specified by the test procedures for determining compliance with the New Source Performance Standards. The test procedure will indicate whether a grab sample or an integrated sample is to be used.

2. Apparatus

2.1 Grab sample (Figure 3-1).

2.1.1 Probe—Stainless steel or Pyrex¹ glass, equipped with a filter to remove particulate matter.

2.1.2 Pump—One-way squeeze bulb, or equivalent, to transport gas sample to analyzer.

¹ Trade name.

2.2 Integrated sample (Figure 3-2)

2.2.1 Probe—Stainless steel or Pyrex¹ glass, equipped with a filter to remove particulate matter.

2.2.2 Air-cooled condenser or equivalent—To remove any excess moisture.

2.2.3 Needle valve—To adjust flow rate.

2.2.4 Pump—Leak-free, diaphragm type, or equivalent, to pull gas.

2.2.5 Rate meter—To measure a flow range from 0 to 0.035 cfm.

2.2.6 Flexible bag—Tedlar¹ or equivalent, with a capacity of 2 to 3 cu. ft. Leak test the bag in the laboratory before using.

2.2.7 Pilot tube—Type S, or equivalent, attached to the probe so that the sampling flow rate can be regulated proportional to the stack gas velocity when velocity is varying with time or a sample traverse is conducted.

2.3 Analysis

2.3.1 Orsat analyzer, or equivalent.

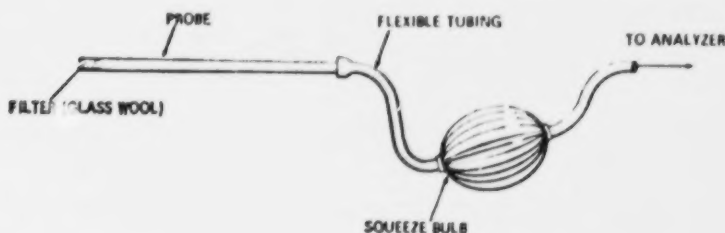


Figure 3-1. Grab-sampling train.

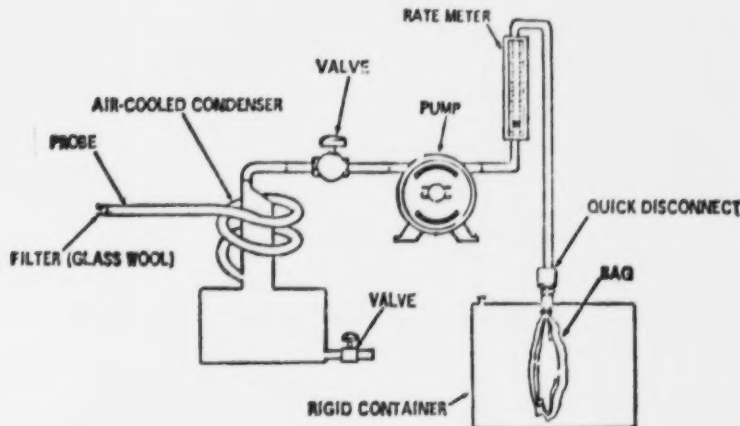


Figure 3-2. Integrated gas-sampling train.

3. Procedure

3.1 Grab sampling

3.1.1 Set up the equipment as shown in Figure 3-1, making sure all connections are leak-free. Place the probe in the stack at a sampling point and purge the sampling line.

3.1.2 Draw sample into the analyzer.

3.2 Integrated sampling

3.2.1 Evacuate the flexible bag. Set up the equipment as shown in Figure 3-2 with the bag disconnected. Place the probe in the stack and purge the sampling line. Connect the bag, making sure that all connections are tight and that there are no leaks.

3.2.2 Sample at a rate proportional to the stack velocity.

3.3 Analysis

3.3.1 Determine the CO, O₂, and CO concentrations as soon as possible. Make as many passes as are necessary to give constant readings. If more than ten passes are necessary, replace the absorbing solution.

3.3.2 For grab sampling, repeat the sampling and analysis until three consecutive samples vary no more than 0.5 percent by volume for each component being analyzed.

3.3.3 For integrated sampling, repeat the analysis of the sample until three consecutive analyses vary no more than 0.2 percent by volume for each component being analyzed.

4. Calculations

4.1 Carbon dioxide. Average the three consecutive runs and report the result to the nearest 0.1% CO₂.

4.2 Excess air. Use Equation 3-1 to calculate excess air, and average the runs. Report the result to the nearest 0.1% excess air.

$C_c EA =$

$$\frac{(C_c O_2 - 0.5(C_c CO))}{0.264(C_c N_2) - (C_c O_2) + 0.5(C_c CO)} \times 100$$

equation 3-1

where:

$C_c EA$ = Percent excess air.

$C_c O_2$ = Percent oxygen by volume, dry basis.

$C_c N_2$ = Percent nitrogen by volume, dry basis.

$C_c CO$ = Percent carbon monoxide by volume, dry basis.

0.264 = Ratio of oxygen to nitrogen in air by volume.

4.3 Dry molecular weight. Use Equation 3-2 to calculate dry molecular weight and average the runs. Report the result to the nearest tenth.

$$M_d = 0.44(C_c CO_2) + 0.32(C_c O_2) + 0.28(C_c N_2 + C_c CO)$$

equation 3-2

where:

M_d = Dry molecular weight, lb/lb-mole.

$C_c CO_2$ = Percent carbon dioxide by volume, dry basis.

$C_c O_2$ = Percent oxygen by volume, dry basis.

$C_c N_2$ = Percent nitrogen by volume, dry basis.

0.44 = Molecular weight of carbon dioxide divided by 100.

0.32 = Molecular weight of oxygen divided by 100.

0.28 = Molecular weight of nitrogen and CO divided by 100.

5. References

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APPENDIX B

GLOSSARY OF SYMBOLS

This is glossary of symbols as used in this document. Symbols used and defined in the reference method (appendix A) are not repeated here.

<u>SYMBOL</u>	<u>DEFINITION</u>
N	Lot size , i.e., the number of field tests to be treated as a group
n	Sample size for the quality audit (section IV)
r	Number of replicate analyses per field test
$CV\{X\}$	Assumed or known coefficient of variation ($100 \sigma_X / \mu_X$)
$\hat{CV}\{X\}$	Computed coefficient of variation ($100 s_X / \bar{X}$) from a finite sample of measurements
σ_X	Assumed standard deviation of the parameter X (population standard deviation)
s_X	Computed standard deviation of a finite sample of measurements (sample standard deviation)
μ_X	Assumed mean value of the parameter X (population mean)
$\bar{X}$	Computed average of a finite sample of measurements (sample mean)
$\hat{\epsilon}_X$	Computed bias of the parameter X for a finite sample (sample bias)
R	Range, i.e., the difference in the largest and smallest values in r replicate analyses
ϵ_X	Random error associated with the measurement of parameter X
$d_j (D_j)$	The difference in the audit value and the value of $M_d (\%CO_2)$ arrived at by the field crew for the j^{th} audit
$\bar{d} (\bar{D})$	Mean difference between $M_d (\%CO_2)$ and $M_{da} (\%CO_2)_a$ for n audits
$s_d (s_D)$	Computed standard deviation of difference between $M_d (\%CO_2)$ and $M_{da} (\%CO_2)_a$
p	Percent of measurements outside specified limits L and U

APPENDIX B

GLOSSARY OF SYMBOLS (CONT'D)

<u>SYMBOL</u>	<u>DEFINITION</u>
k	Constant used in sampling by variables (section IV)
ϵ	A positive number used to calculate the required number of replicate analyses such that the error in estimating $\%CO_{2t}$ by the mean of r replicates will be less than ϵ .
P{Y}	Probability of event Y occurring
t	Statistic used to determine if the sample bias, $\bar{d}$, is significantly different from zero (t-test)
χ^2	Statistic used to determine if the sample variance, s^2 , is significantly different from the assumed variance, σ^2 , of the parent distribution (chi-square test)
$\Phi(\epsilon/\sigma)$	Area under a standard normal curve to the left of (or less than) the value ϵ/σ
L	Lower quality limit used in sampling by variables
U	Upper quality limit used in sampling by variables
CL	Center line of a quality control chart
LCL	Lower control limit of a quality control chart
UCL	Upper control limit of a quality control chart

APPENDIX C

GLOSSARY OF TERMS

The following glossary lists and defines the statistical terms as used in this document.

Accuracy	A measure of the error of a process expressed as a comparison between the measured value and the true value.
Bias	The systematic or nonrandom component of system error.
Lot	A specified number of objects to be treated as a group.
Measurement Method	A set of procedures for making a measurement.
Measurement Process	The process of making a measurement including method, personnel, equipment, and environmental conditions.
Population	A very large number of like objects (i.e., measurements, checks, etc.) from which the true mean and standard deviation can be deduced with a high degree of accuracy.
Precision	The degree of variation among measurements on a homogeneous material under controlled conditions, and usually expressed as a standard deviation or, as is done here, as a coefficient of variation.
Quality Audit	A management tool for independently assessing data quality.
Quality Control Check	Checks made by the field crew on certain items of equipment and procedures to assure data of good quality.
Sample	Objects drawn usually at random from the lot for checking.